POLYMERIC SULFUR-, PHOSPHORUS-, CARBON - NITROGEN - COMPOUNDS

R. APPEL, G. EISENHAUER, H. GERBER, et. al.

ANORGANISCH-CHEMISCHES INSTITUT
DER UNIVERSITÄT HEIDELBERG, GERMANY

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FOREWORD

This report was prepared by the Messrs. R. Appel, G. Eisenhauer, H. Gerber, A. Hauss, W. Heinzelmann, and H. Rittersbacher of the Anorganisch-Chemisches Institut der Universität Heidelberg, Germany, under USAF Contract No. AF 61(052)-361. The contract was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena," Task No. 734201, "Basic Factors on the Synthesis of Macromolecular Materials." The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, Dr. W. L. Lehn, Project Engineer.

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This technical report has been reviewed and is approved.

William E. Gibbs

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ABSTRACT

The following bi-functional compounds were synthesized as starting materials for the synthesis of inorganic polymers with sulphur-nitrogen-carbon bonds:

Sulfuryl-diisocyanate, $O_2S(NCO)_2$; amidosulfuric acid isocyanate, H_2NSO_2NCO; chlorosulfuryl-isocyanate, $ClSO_2NCO$; fluorosulfuryl-isocyanate, FSO_2NCO; imido-bis-sulfuric acid chloride, $HN(SO_2Cl)_2$, and imido-bis-sulfuric acid fluoride, $HN(SO_2F)_2$. The polyaddition of diamines and diols with $O_2S(NCO)_2$ results in polymers which are not very stable to temperature and hydrolysis. The polymers found by reaction of H_2NSO_2NCO with urea and sulfamide, $O_2S(NH_2)_2$, likewise, are not very stable.

In the field of the phosphorus-nitrogen-compounds the synthesis of triphenylphosphine-imines and of N-halogen-phosphine imines is described. The reaction of halogen-imines with triply-bounded phosphorus derivatives is leading to compounds with the system of $\geq P\text{-}\underline{N}\text{-}P\leq$. Further experiments deal with antimony-nitrogen compounds and their reactions.

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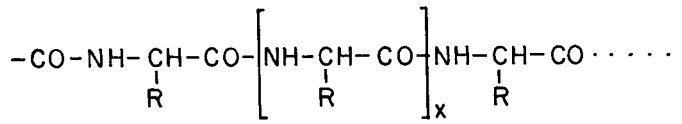
SECTION I

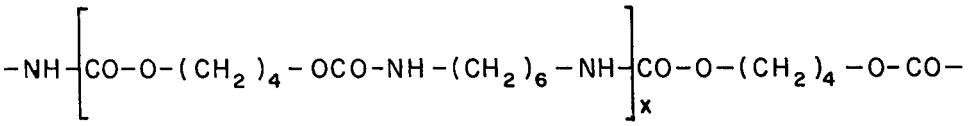
INTRODUCTION

It is well known that natural silk consists of polypeptide chains formed by condensation of amino acids. This reaction mechanism leads to formation of long-chain molecules, consisting of a repetition of monomeric units connected by a carbonamide linkage:



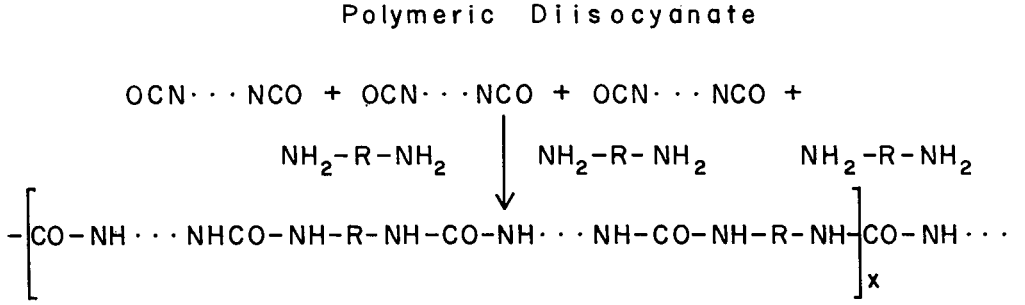
(1)

Synthetic modifications of the above structure have been prepared in an attempt to duplicate the physical properties of silk. Worthy of mention is the fundamental work of Otto Bayer (Reference 1), who was able to prepare spinnable polyurethanes through addition polymerization of organic diisocyanates with diglycols. For example, it was possible to make the so-called Perlon U by polymerization of hexamethylene diisocyanate with tetramethylene diglycol, having the following structure:



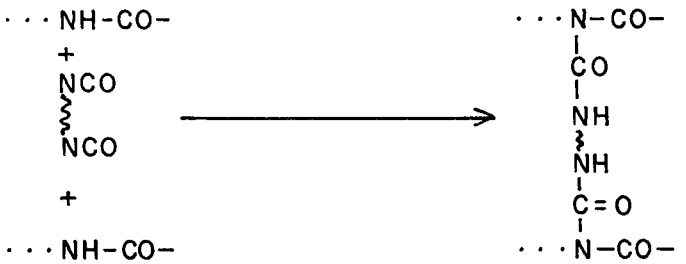
(2)

This reaction was subsequently carried out in the presence of a small excess of diisocyanate, resulting in macromolecules with terminal isocyanate groups. By means of the so-called Vulkollan (Reference 2) process, these macromolecular diisocyanates are joined together with organic diamines to still longer chains:



(3)

Reaction of macromolecular diisocyanates with the free NH groups in the chain leads to branching and cross-linking via allophanate groups:



(4)

It was of interest to determine if similar polymers could be formed from inorganic isocyanates such as sulfuryl diisocyanate, $SO_2(NCO)_2$, phosphoryl triisocyanate, $PO(NCO)_3$, or the halogen sulfuryl isocyanates. Accordingly we sought suitable preparative methods for polymeric sulfuryl urethanes, monosulfuryl ureas, disulfuryl ureas, and phosphoryl ureas. In addition, we concerned ourselves with the preparation and properties of polymeric phosphorus-nitrogen and antimony-nitrogen compounds.

Our initial task was to find means for making available, in larger quantities, the starting materials for these polymers. The results of our efforts are reported.

SECTION II

EXPERIMENTS ON THE PREPARATION OF BIFUNCTIONAL SULFURIC ACID DERIVATIVES FOR USE IN MIXED INORGANIC-ORGANIC POLYMERS

Sulfuryl Diisocyanate $O_2S(NCO)_2$

As already mentioned in the Introduction, organic diisocyanates have long been used as starting materials for the preparation of polymers. On the other hand, literature on inorganic diisocyanates was meager and their reactions relatively unknown. Therefore, we first sought a suitable process for preparing sulfuryl diisocyanate, with the aim of polymerizing this inorganic diisocyanate with diglycols to polymeric sulfuryl urethanes, and with amines to polymeric sulfuryl ureas.

Our first successful preparation of sulfuryl diisocyanate was through metathesis of chlorosulfuryl isocyanate with silver isocyanate:

$$ClSO_2NCO + AgNCO \longrightarrow SO_2(NCO)_2 + AgCl \qquad (5)$$

Good yields are achieved. Sulfuryl diisocyanate is a mobile, colorless liquid with a normal boiling point of 139°C and a melting point of -5°C.

Although chlorosulfuryl isocyanate is easily prepared by the Graf method (Reference 3) from cyanogen chloride and sulfur trioxide,

$$ClCN + SO_3 \longrightarrow ClSO_2NCO \qquad (6)$$

the use of silver cyanate for preparing larger amounts of sulfuryl diisocyanate cannot be considered because of the expense.

Further investigation showed that sulfuryl diisocyanate can also be made from the much cheaper potassium cyanate. In the reaction of potassium cyanate with sulfur trioxide, there forms initially potassium disulfate and disulfuryl diisocyanate:

$$2\,KOCN + 4SO_3 \longrightarrow K_2S_2O_7 + S_2O_5(NCO)_2 \qquad (7)$$

The latter breaks down thermally at 140°C into sulfur trioxide and sulfuryl diisocyanate:

$$S_2O_5(NCO) \xrightarrow{140°C} SO_2(NCO)_2 + SO_3 \qquad (8)$$

However, the best process for sulfuryl diisocyanate is the reaction of sulfur trioxide with cyanogen bromide to give bromine, sulfur dioxide, and disulfuryl diisocyanate, the latter then being decomposed pyrolytically to sulfur trioxide and sulfuryl diisocyanate:

$$2\,BrCN + 3SO_3 \longrightarrow S_2O_5(NCO)_2 + Br_2 + SO_2 \qquad (9)$$

$$S_2O_5(NCO)_2 \xrightarrow{heat} SO_2(NCO)_2 + SO_3 \qquad (10)$$

Reaction of Sulfuryl Diisocyanate

The reactivity of sulfuryl diisocyanate is determined primarily by the two isocyanate groups. For example, with excess water, the compound hydrolyzes as expected to give sulfamide. The reaction proceeds over the following intermediate steps:

$$O_2S\begin{matrix}\diagup N=C=O \\ \diagdown N=C=O\end{matrix} + 2H_2O \longrightarrow O_2S\begin{matrix}\diagup NH\text{-}COOH \\ \diagdown NH\text{-}COOH\end{matrix} \xrightarrow{-2CO_2} O_2S\begin{matrix}\diagup NH_2 \\ \diagdown NH_2\end{matrix} \qquad (11)$$

We therefore considered the possibility of converting sulfuryl diisocyanate with water in a 1:1 mole ratio, in a suitable solvent, to amidosulfuric acid isocyanate:

$$O=C=N-SO_2-N=C=O + H_2O = H_2N-SO_2-N=C=O + CO_2 \qquad (12)$$

Our experiments with solutions in benzene or in acetonitrile actually did show that a partial hydrolysis is possible, yielding amidosulfuric acid isocyanate, according to Equation 12. After adding exactly 1 mole water per mole sulfuryl diisocyanate in acetonitrile, a clear solution forms containing, initially, the monomeric form of amidosulfuric acid isocyanate. It is, however, not surprising that amidosulfuric acid isocyanate, as a bifunctional molecule with a sulfonamide and an isocyanate group, easily self-polymerizes to polysulfuryl ureas of the type $NH_2\text{-}(SO_2NHCONH)_x SO_2NCO$ (I). In fact, we were unable to obtain monomeric amidosulfuric acid isocyanate free of solvent. Even very rapid removal of the solvent acetonitrile at -5 to -10°C caused mainly separation of an oil, which solidified within a few minutes. The solid was probably the polymeric compound $H_2N\text{-}(SO_2\text{-}NH\text{-}CO\text{-}NH)_x\text{-}SO_2\text{-}N=C=O$, where x is 10 to 12.

Determination of the half-life of monomeric amidosulfurinc acid isocyanate was possible on the basis of the following considerations and experiments:

Hydrolysis of amidosulfuric acid isocyanate yields sulfamide, according to Equation 13:

$$H_2N-SO_2-NCO + H_2O \longrightarrow H_2N-SO_2-NH_2 + CO_2 \qquad (13)$$

Sulfamide is neutral in water. In the hydrolysis of the polymeric product I, on the other hand, polymeric sulfuryl ureas were to be expected.

$$H_2N(SO_2NHCONH)_x SO_2NCO + H_2O = H_2N(SO_2NHCONH)_x SO_2NH_2 + CO_2 \qquad (14)$$

The polymeric product formed according to the hydrolysis reaction (14) contains one very acid proton per monomeric unit, $-SO_2-NH-CO-NH-$, which can be titrated with methyl orange, assuming a sufficiently high polymerization grade. This can be ascribed to the prototropic effect of the SO_2 group.

On the basis of this acidity, the polymerization could be followed by a simple acidometric titration. For this purpose, solutions of amidosulfuric acid isocyanate in acetonitrile were prepared, from which aliquot samples were removed from time to time. These were immediately sprayed into water to destroy the amidosulfuric acid isocyanate which had not yet polymerized. Subsequent titration permitted determination of the number of $-SO_2NH-CO-NH-$ units. In the graphical evaluation of these data, the reaction time was plotted against the titer (both as logarithm and as reciprocal). The results showed that, following an initiation period of 125 minutes, the logarithmic and not the reciprocal plot was linear, which means that during this period the polymerization was a first order reaction, i.e., each monomeric amidosulfuric acid isocyanate molecule adds to the end of the long polysulfuryl urea chain. The reaction rate constant was determined from the slope of the logarithmic plot on the linear portion between 150 and 550 minutes. The value $k^I(25°C)$ was found to be $1{,}11 \times 10^{-3}$ min^{-1}, giving a half-life of 623 minutes for amidosulfuric acid isocyanate. The results of these kinetic studies show that freshly prepared amidosulfuric acid isocyanate has a rather long life, so that preparative reactions with this compound in solutions are possible.

We now describe a series of reactions which provide chemical evidence for the existence of the monomeric form of amidosulfuric acid isocyanate in solution. If gaseous ammonia is passed through a freshly prepared acetonitrile solution of H_2N-SO_2-NCO, a crystalline substance forms which melts at 123°C and which could be characterized as the ammonium salt of urea sulfonamide. Presumably the substance forms according to Equation 15:

$$H_2N-SO_2-NCO + 2NH_3 \longrightarrow NH_4(H_2N-SO_2-NH-CO-NH_2) \qquad (15)$$

The structure of this compound was determined by analysis, molecular weight, and hydrolytic decomposition.

Further proof for the relative stability of monomeric amidosulfuric acid isocyanate in a freshly prepared acetonitrile solution was given by its reaction with alcohol according to Equation 16:

$$H_2N-SO_2-NCO + C_2H_5OH \rightarrow H_2N-SO_2-NH-CO-OC_2H_5 \qquad (16)$$

The amidosulfuryl urethane is obtained in a 90 percent yield. It is the first member of a class of compounds hitherto unknown. As with all urethanes, it crystallizes well, forming needles several centimeters long. The melting point is very sharp at 143.5°C.

If one reacts a freshly prepared solution of H_2NSO_2NCO in acetonitrile at room temperature with the readily available 2,4-dinitrophenyl hydrazine, there forms a product according to Equation 17:

$$H_2N-SO_2NCO + H_2N-NH-C_6H_3(NO_2)_3 \longrightarrow H_2N-SO_2-NH-CO-NH-NH-C_6H_3(NO_2)_2 \qquad (17)$$

with a yield of 90 percent. Melting point is 168°C. Analysis, molecular weight, and chemical properties showed the product to be 1-dinitrophenyl-4-amidosulfuryl semicarbazide. The yellow substance is rather insoluble in cold water, giving a weak acid solution. Acetone and alcohol are good solvents for the compound. Boiling a 10 percent aqueous solution for 10 minutes causes quantitative decomposition to sulfamide, carbon dioxide, and 2,4-dinitrophenyl hydrazine:

$$H_2N\text{-}SO_2\text{-}NH\text{-}CO\text{-}NH\text{-}NH\text{-}C_6H_3(NO_2)_2 + H_2O \longrightarrow O_2S(NH_2)_2 + CO_2 + H_2N\text{-}NH\text{-}C_6H_3(NO_2)_2 \quad (18)$$

It is worth noting that a color change from light yellow to dark brown occurs when caustic is added, even in very dilute solutions. Because of this very clear and obvious color change, 1-dinitro-phenyl-4-amidosulfuryl semicarbazide can function as an acid-base indicator. By potentiometric titration we determined the dissociation constant of the indicator acid as $K_{HInd} = 2.5 \times 10^{-5}$.

Activation of the isocyanate group by the neighboring SO_2-group is so great, that amidosulfuric acid isocyanate also reacts with the otherwise proton-inactive acid amides. It was actually possible to obtain amidosulfuryl biuret by reacting amidosulfuric acid isocyanate with urea, according to Equation 19:

$$NH_2\text{-}SO_2\text{-}NCO + NH_2CONH_2 \rightarrow \underset{\text{II}}{NH_2\text{-}SO_2NH\text{-}CO\text{-}NH\text{-}CO\text{-}NH_2} \quad (19)$$

In this reaction, only one amide group of urea reacts with the amidosulfuric acid isocyanate. Yield of the biuret derivative is 90 percent. The compound has a melting point of 158°C, is difficultly soluble in cold water, forming a strongly acid solution. In the same way, thiourea could be reacted with amidosulfuric acid isocyanate to give amidosulfuryl thiobiuret.

In sulfamide, the amide hydrogens are more strongly activated by the SO_2-group than are the amide hydrogens in urea. Therefore, it is not surprising that sulfamide can react, according to Equation 20, with two moles amidosulfuric acid isocyanate to form sulfuryl diurea-sulfurylamide (III):

$$NH_2SO_2NH_2 + NH_2SO_2NCO \longrightarrow \underset{\text{III}}{SO_2(NHCONHSO_2NH_2)_2} \quad (20)$$

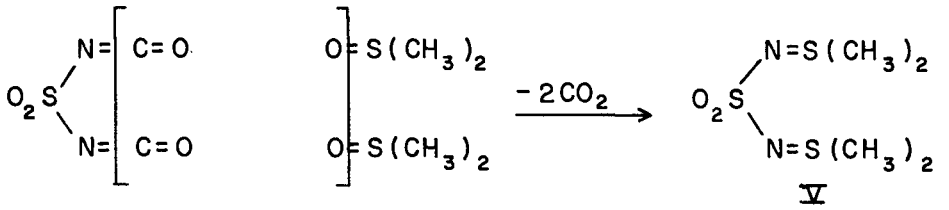
The raw product melts between 160° and 170°C; yield is 75 percent of theory. This product, by recrystallizing three times in water, could be hydrolytically decomposed to urea disulfonic acid amide, $NH_2SO_2NHCONHSO_2NH_2$ (IV), sulfamide, and carbon dioxide.

By proper choice of reaction conditions, amidosulfuric isocyanate and sulfamide could be reacted directly in aqueous acetonitrile to give urea disulfonic acid amide (IV). This compound melts at 152°C. Because of the prototropic effect of the SO_2-group, the compound is very acid and dissociates according to Equation 21:

$$H_2NSO_2NHCONHSO_2NH_2 \rightleftharpoons (NH_2SO_2NHCONSO_2NH_2)^- + H^+ \quad (21)$$

The proton can be titrated against methyl orange.

Thus far, we have covered the complete hydrolysis of sulfuryl diisocyanate to sulfamide, the partial hydrolysis to amidosulfuric acid isocyanate, as well as the reactions of the latter. It remains only to mention in conclusion an interesting reaction of sulfuryl diisocyanate with dimethyl sulfoxide; surprisingly, a very lively reaction takes place. We were able to establish that the following occurs:



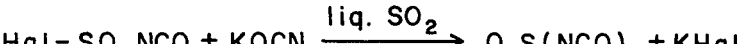
(22)

V

The compound V crystallizes well; it melts at 153°C.

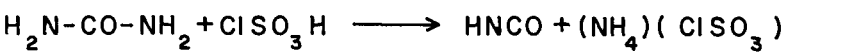
Chlorosulfuryl Isocyanate

In our studies of the reactive sulfuryl isocyanates, we also included the halogen sulfuryl isocyanates because our previous experience showed that chlorosulfuryl isocyanate could be converted with silver cyanate to sulfuryl diisocyanate (Equation 5), a process which is ruled out commercially only by the high cost of the silver salt. In addition, it seemed to us that halogen sulfuryl isocyanate might possibly react with the much cheaper potassium cyanate in liquid sulfur dioxide to give sulfuryl diisocyanate.



(23)

Finally, the halogen sulfuryl isocyanates are themselves very reactive, bifunctional molecules, whose use in inorganic polymer chemistry could lead to interesting results. Therefore, we first sought a suitable process to make chlorosulfuryl isocyanate which could eventually compete with the method of R. Graf (Reference 3) (cyanogen chloride and sulfur trioxide, Equation 6). We found a convenient synthesis, with inexpensive starting materials, in the reaction of urea with chlorosulfonic acid. First, isocyanic acid is formed, which then reacts further with chlorosulfonic acid to chlorosulfuryl isocyanate.



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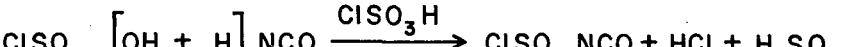
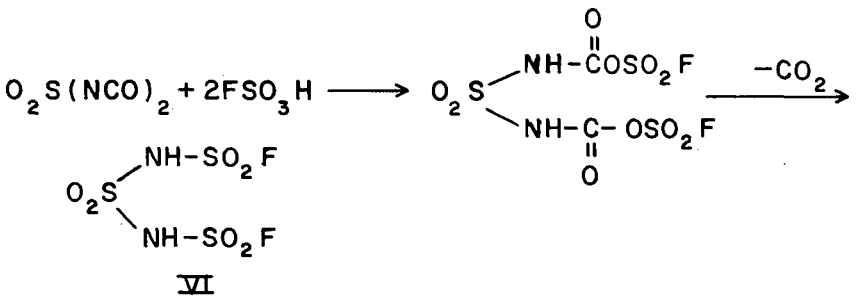


(25)

Fluorosulfuryl Isocyanate

New synthesis was found for fluorosulfuryl isocyanate in the reaction of sulfuryl diisocyanate with fluorosulfonic acid. Surprisingly, the reaction does not proceed according to Equation 26, as one would expect from the normal behavior of isocyanate groups, to form VI:



(26)

VI

but rather the primary step is an exchange of the isocyanate group for a fluorine atom:

$$OCNSO_2NCO + HOSO_2F \longrightarrow OCNSO_2OH + OCNSO_2F \qquad (27)$$

forming fluorosulfuryl isocyanate and sulfuric acid monoisocyanate. This reaction is favored by the volatility of fluorosulfuryl isocyanate, which distills rapidly out of the reaction mixture before it can react any further.

Imidobis-Sulfuric Acid Chloride

The halogen sulfuryl isocyanates, $X\text{-}SO_2\text{-}NCO$, provided us with excellent starting materials for the preparation of imido bis-sulfuric acid halides, $X\text{-}SO_2\text{-}NH\text{-}SO_2\text{-}X$.

Although chlorosulfuryl isocyanate and chlorosulfonic acid do not react at room temperature, equimolecular amounts at reflux slowly but steadily release carbon dioxide. This decarboxylation proceeds according to the following reaction:

$$ClSO_2NCO + HOSO_2Cl \longrightarrow Cl\text{-}SO_2\text{-}N(H)\text{-}C(=O)\text{-}O\text{-}SO_2Cl \xrightarrow{-CO_2} HN(SO_2Cl)_2 \qquad (28)$$

If the heating is continued until gas evolution ceases, the reaction vessel then contains almost pure imido bis-sulfuric acid chloride. Subsequent purification by vacuum distillation is possible. Yield of the analytically pure product, based on Equation 28, is 70 percent. The compound melts at 37°C and boils in high vacuum at 55°C; refractive index is $n_D^{25} = 1.4948$.

The reaction of chlorosulfuryl isocyanate with chlorosulfonic acid to imido bis-sulfuric acid chloride also provided us with an explanation of the observed fact, that one mole urea reacts with three moles chlorosulfonic acid to imido bis-sulfuric acid chloride, besides ammonium hydrogensulfate, hydrogen chloride, and carbon dioxide, according to the overall equation:

$$OC(NH_2)_2 + 3ClSO_3H \longrightarrow HN(SO_2Cl)_2 + [NH_4]HSO_4 + HCl + CO_2 \qquad (29)$$

One can imagine this overall reaction occurring by the following steps. First, urea splits off ammonia to yield isocyanic acid:

$$OC(NH_2)_2 \longrightarrow HN{=}C{=}O + NH_3 \qquad (30)$$

Isocyanic acid is sulfonated by chlorosulfonic acid; in the presence of ammonia, ammonium hydrogensulfate and hydrogen chloride are also formed:

$$O=C=NH + 2HOSO_2Cl + NH_3 \longrightarrow O=C=N-SO_2Cl + HCl + [NH_4]HSO_4 \quad (31)$$

The chlorosulfuryl isocyanate so formed reacts further with chlorosulfonic acid to carbon dioxide and imido bis-sulfuric acid chloride, Equation 28.

A further possibility for preparing imido bis-sulfuric acid chloride is based on the reaction of phosphorus pentachloride with sulfamic acid, in which trichlorophosphazosulfuric acid chloride initially forms:

$$2\,PCl_5 + H_2N-SO_3H \longrightarrow Cl_3P=N-SO_2Cl + POCl_3 + 3HCl \quad (32)$$

The latter can react further with chlorosulfonic acid at 80°C to give imido bis-sulfuric acid chloride and phosphorus oxytrichloride:

$$Cl_3P=N-SO_2Cl + ClSO_3H \longrightarrow HN(SO_2Cl)_2 + POCl_3 \quad (33)$$

Imidobis-Sulfuric Acid Fluoride

Preparation of imido bis-sulfuric acid fluoride, $HN(SO_2F)_2$, proceeds by methods analogous in principle with those for the corresponding chloride already described. For one, fluorsulfonic acid reacts by heating with fluorosulfuryl isocyanate in equimolar amounts with decarboxylation and formation of imido bis-sulfuric acid fluoride, Equation 34:

$$F-SO_2NC=O + FSO_3H \longrightarrow F-SO_2-\underset{\displaystyle H}{\overset{\displaystyle |}{N}}-\overset{\displaystyle O}{\overset{\displaystyle ||}{C}}-O-SO_2F \xrightarrow{-CO_2} HN\begin{matrix}\diagup SO_2F \\ \diagdown SO_2F\end{matrix} \quad (34)$$

The product is obtained in 70 to 75 percent yield in very pure form. It melts at +17°C.

Imido bis-sulfuric acid fluoride is also obtained, in 60 percent yield from urea and fluorosulfonic acid (1:3 mole ratio) according to Equation 35:

$$O=C(NH_2)_2 + 3HOSO_2F \longrightarrow HN(SO_2F)_2 + [NH_4][HSO_4] + HF + CO_2 \quad (35)$$

The mechanism is the same as in the formation of imido bis-sulfuric acid chloride from urea and chlorosulfonic acid (Equations 28, 30, and 31). This latter method is, however, less convenient than that starting from fluorosulfuryl isocyanate and fluorosulfonic acid, Equation 34.

SECTION III

EXPERIMENTS ON THE PREPARATION OF POLYMERIC SULFURYL URETHANES AND POLYMERIC SULFURYL UREAS

Reaction of Sulfuryl Diisocyanate with Ethylene Glycol

Referring to the fundamental work of Otto Bayer (Reference 1), who was able to obtain spinnable polyurethanes through addition polymerization of organic diisocyanates with diglycols, Equation 2, we reacted sulfuryl diisocyanate with ethylene glycol, hoping to obtain polymeric sulfuryl urethanes.

If one carries out the reaction of sulfuryl diisocyanate with glycol in the presence of benzene as the solvent, a gelatinous, benzene-insoluble product is obtained, showing all the properties of a polymeric sulfuryl urethane:

$$n\,SO_2(NCO) + n\,HO-CH_2-CH_2OH \longrightarrow +SO_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-NH+_n \qquad (36)$$

The polymeric product is insoluble in cold benzene, water, acetone, nitrobenzene, alcohols, and acetonitrile; it is quite soluble in dimethylformamide, in which it forms very viscous solutions.

If an excess of glycol is used in the preparation, the main product is the linear compound VII:

$$HO-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-NH-(SO_2NH-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-NH)_n-SO_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-OH$$

VII

n = 3 Fp 169°

This poly-(sulfuryl urethane) is a granular, horn-like substance with a sharp melting point at 169°C; it is likewise soluble only in dimethylformamide.

Reaction of Sulfuryl Diisocyanate with Ethylene Diamine

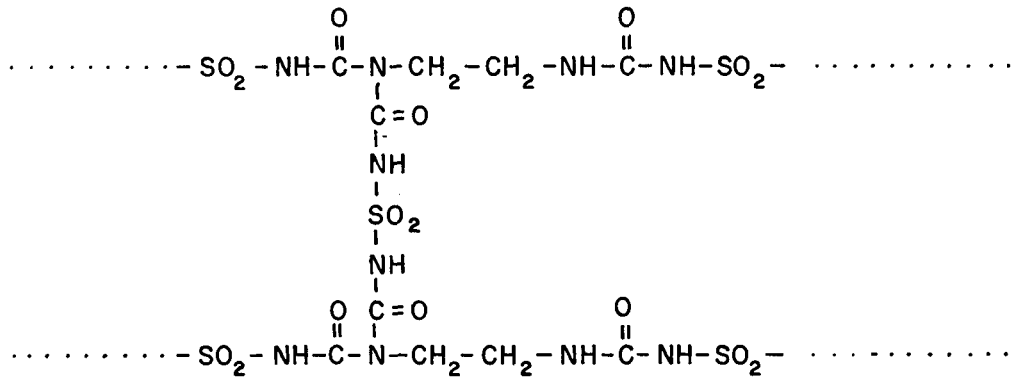
First, it was attempted to form poly- (sulfuryl ureas) by reacting sulfuryl diisocyanate with ethylene diamine. In benzene, the reaction is exothermic and requires external cooling. A solid, white mass is obtained, insoluble in benzene and numerous other organic solvents. Like other polyureas, however, the substance is hydrophilic and quite soluble in water. Precipitation out of a water solution by addition of acetone serves as a purification method. From the analysis and qualitative properties, it must be concluded that the polymerization does not yield a linear poly-(sulfuryl urea), but rather a cross-linked polymer. Supposedly, linear chains are initially formed, according to Equation 37:

$$OCN-SO_2-NCO + H_2N-CH_2-CH_2-NH_2 + OCN-SO_2^- \cdots\cdots\cdots$$

$$\downarrow$$

$$-SO_2-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-CH_2-CH_2-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-SO_2-\cdots\cdots\cdots\cdots\cdots \qquad (37)$$

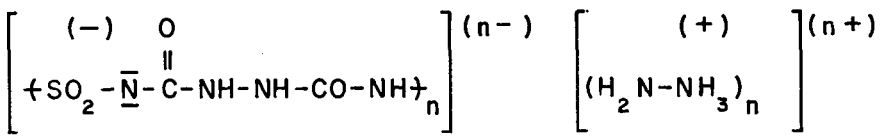
However, since the ureas groups can also react further with isocyanate groups, the chains become cross-linked. At the points of cross-linkage, the structure is as follows:



This disorderly, cross-linked structure is the reason for the unsharp melting point observed. The product softens at 150 to 170°C, with simultaneous decomposition.

Reaction of Sulfuryl Diisocyanate with Hydrazine

Using hydrazine as the diamine gives entirely different results. Initially, linear polymers are probably formed, but due to the prototropic effect of the SO_2-groups, the neighboring hydrogens are acid and react further with hydrazine to form salts. Analysis, infrared spectrum, and the relative amounts of free and bound hydrazine indicate the following structure:



If the reaction is carried out in anhydrous acetonitrile as solvent, the raw product is first obtained as an oil, which solidifies after a time to a glass melting at 154°C, with decomposition.

In the reaction of sulfuryl diisocyanate with hydrazine, it made no difference which reactant was in excess; they always combined in the mole ratio 1:2 to give the same glass-like polymer.

SECTION IV

EXPERIMENTS ON THE PREPARATION OF POLYFUNCTIONAL DERIVATIVES OF PHOSPHORIC ACID

Phosphoryl Triisocyanate

At the conclusion of our investigations of the isocyanates of sulfuric acid, we turned to a study of phosphoric acid isocyanates. Our first success was the preparation of phosphoryl triisocyanate from silver cyanate and phosphorus oxytrichloride. It is a colorless substance which can be vacuum-distilled without decomposition. Although this method is not commercially feasible, we used it anyway in order to obtain enough product to study its properties.

Our next step was the preparation of monomeric isocyanic acid by depolymerization of cyanuric acid:

$$(-CO-NH-)_3 \xrightarrow{\text{Heat}} 3HN=C=O \qquad (38)$$

This depolymerization depends strongly on the purity of the cyanuric acid used. We found that suitable cyanuric acid can be prepared by heating urea with amyl alcohol. From cyanuric acid prepared in this way, it was possible to obtain monomeric isocyanic acid which was not so sensitive to self-polymerization and whose solutions in chlorohydrocarbons or in ether could be kept for longer periods of time.

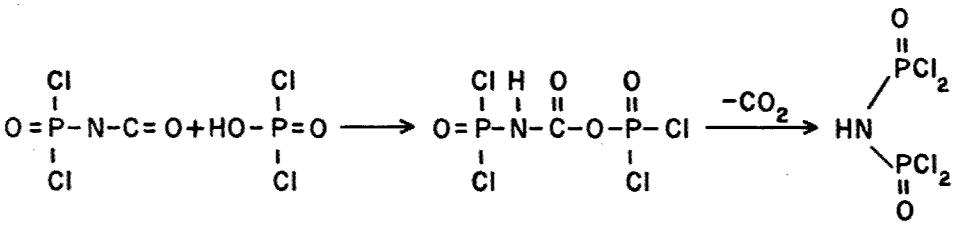
Isocyanic acid was prepared for the purpose of reacting it further with phosphorus oxytrichloride to give phosphoryl triisocyanate, according to Equation 39:

$$POCl_3 + 3HNCO = OP(NCO)_3 + 3HCl \qquad (39)$$

We were able to carry out the reaction in the presence of a weak base; the yields of triisocyanate, however, were poor.

Reaction of Dichlorophosphoryl Isocyanate with Dichlorophosphoric Acid

In the area of phosphoric acid isocyanate, we considered dichlorophosphoryl isocyanate, $OPCl_2NCO$, since we hoped that it would react with dichlorophosphoric acid to give, according to Equation 40, imido bis-phosphoryl dichloride:



(40)

However, contrary to the success achieved with the analogous sulfur compound, this reaction did not go. There is evolution of HCl; carbon dioxide forms only in small amounts. At the higher temperatures necessary for decarboxylation, the main reaction becomes a self-condensation of dichlorophosphoric acid to polymeric phosphoryl chlorides.

Reaction of Phosphorus Pentachloride with Hydroxylamine in Presence of Triphenyl Phosphine

If one reacts hydroxylamine with phosphorus pentachloride, imene is formally formed, as in the Lossen Reaction with splitting out of water:

$$NH_2OH + PCl_5 \longrightarrow NH + POCl_3 + 2HCl \qquad (41)$$

Imene can be captured by triphenylphosphine, forming triphenylphosphine-imine:

$$Ph_3P + NH \longrightarrow Ph_3P = NH \qquad (42)$$

which immediately reacts further with phosphorus oxytrichloride, according the the following equation:

$$Ph_3PNH + POCl_3 \longrightarrow Ph_3P = \bar{N}-\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{P}} = O + HCl \qquad (43)$$

Besides this main product, there was a salt-like by-product which probably has the structure:

$$\left[Ph_3P-\underline{\bar{N}}-PPh_3\right]^+ \left[\begin{array}{cc} Cl & Cl \\ | & | \\ O=P-\underline{\bar{N}}-P & =O \\ | & | \\ Cl & Cl \end{array}\right]^-$$

Analysis, infrared spectrum and molecular weight are in agreement with this formulation. The anion of this salt is a derivative of the desired imido bis-phosphoryl dichloride, $HN(POCl_2)_2$.

SECTION V

PHOSPHORUS-NITROGEN DERIVATIVES OF PHOSPHINE IMINES

Triphenylphosphine Imine and N-Halogen Phosphine Imines

In the area of phosphorus-nitrogen chemistry, we turned to the class of phosphine imines, in the hopes of finding new starting materials for preparation of phosphorus-nitrogen polymers. We began our studies with triphenylphosphine-iminium chloride, which can be prepared from chloramine and triphenylphosphine in ether:

$$Ph_3P + NH_2Cl \longrightarrow \left[Ph_3PNH_2\right]Cl \qquad (44)$$

Triphenylphosphine-iminium chloride can be deprotonated with sodamide in liquid ammonia to the free triphenylphosphine imine:

$$\left[Ph_3PNH_2\right]Cl + NaNH_2 \xrightarrow[NH_3]{liq.} Ph_3P=NH + NaCl + NH_3 \qquad (45)$$

which melts at 126°C and can be distilled in vacuum without decomposition. Heating under normal pressure causes benzene to split off; polymers of the type $\left\{(C_6H_5)_2P=\overline{N}-\right\}_x$ are formed, which easily solidify. Their softening point is about 60°C; at 100°C, a viscous melt forms.

Reaction of triphenylphosphine imine with halogens yields the corresponding N-halogen phosphine imines:

$$Ph_3P=N-H + X_2 \xrightarrow{-HX} Ph_3P=N-X \qquad (46)$$

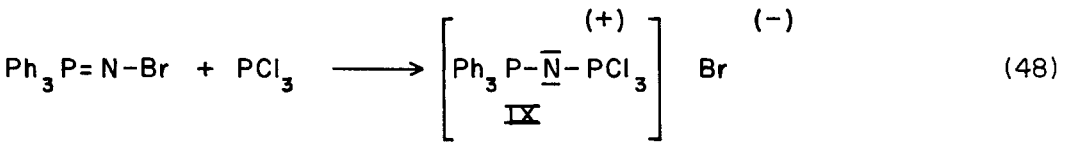
The triphenylphosphine-N-chlorimine, prepared according to Equation 46, splits out chlorobenzene when heated over its melting point; polymeric phosphornitrilic compounds result.

Reaction of N-Halogen Phosphine Imines with Trivalent Phosphorus Compounds

A hitherto unknown way to prepare new phosphorus-nitrogen compounds is the reaction of N-halogen phosphine imines with tertiary phosphines. For example, triphenyl-phosphine N-bromoimine reacts with triphenyl phosphine, Equation 47, to the salt-like compound VIII:

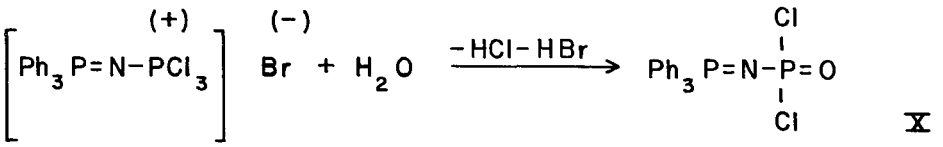
$$Ph_3P=N-Br + Ph_3P \rightarrow \left[Ph_3P-\underset{\text{VIII}}{\overline{\underline{N}}}-Pph_3\right]Br \qquad (47)$$

This reaction of N-halogen phosphine imine is generally applicable to all compounds of trivalent phosphorus, including phosphites and phosphorus trichloride. Reaction with the latter provides a good example:



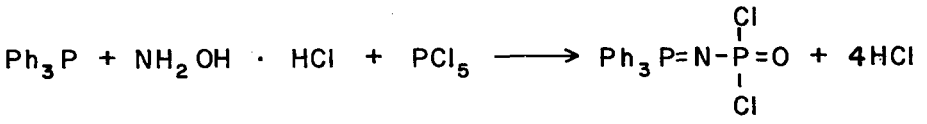
(48)

Because of the formal positive charge on the second phosphorus atom, Compound IX is vulnerable to nucleophilic attack by water, whereby two moles of hydrogen halide split off and Compound IX is converted to the very stable triphenylphosphine imine dichlorophosphate, Compound X:



(49)

Compound X is identical with the main product obtained in the reaction between hydroxylamine hydrochloride and phosphorus pentachloride in the presence of triphenylphosphine, according to the overall reaction, Equation 50:

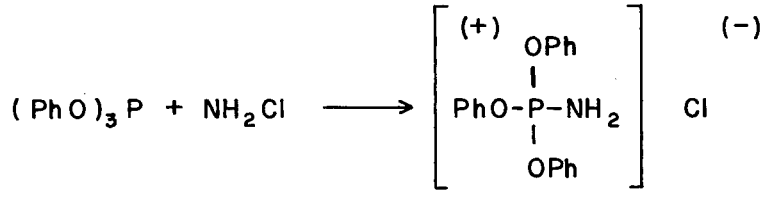


(50)

(Concerning the individual steps in this reaction, see Equations 41, 42, and 43.)

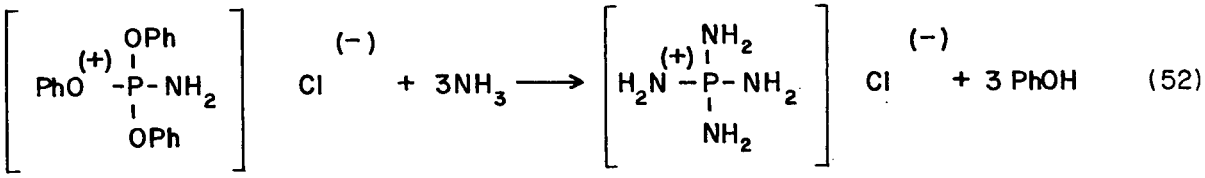
Reaction of Triphenyl Phosphite with Chloramine

It should be mentioned that the primary step in the reaction of triphenyl phosphite with chloramine is exactly the same as with triphenyl phosphine and chloramine:



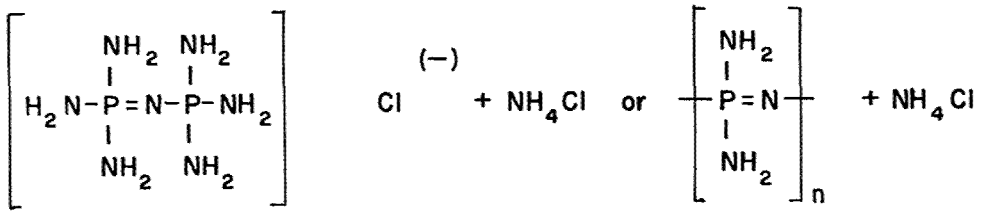
(51)

With excess ammonia, this triphenoxy-phosphineiminium chloride splits out phenol and forms a totally inorganic compound, Equation 52:



(52)

It has not yet been determined if this compound really has the structure of a tetra-amido phosphinium salt. It could also be a mixture such as one of the following, having the same composition.



SECTION VI

ANTIMONY-NITROGEN COMPOUNDS

As is well known, members of the higher periods of the periodic table have a greater tendency to form polymeric compounds than do those of the lower periods. Based on this consideration, we sought to prepare stibine imines, $R_3Sb{=}\bar{N}H$, the antimony analogues of phosphine imines.

This is not possible by reacting triaryl stibines with chloramine and subsequent deprotonation of the iminium chloride to free base. However, a successful synthesis proceeds according to Equation 53, the reaction of triaryl stibine dichlorides with sodamide or potassium amide in a sealed tube:

$$R_3SbCl_2 + 2NaNH_2 = R_3Sb = NH + 2NaCl + NH_3 \qquad (53)$$

An interesting new synthetic route was found for the starting materials, the triaryl stibine dichlorides. It depends on the reaction of the readily available stibine oxides with phosgene:

$$R_3SbO + OCCl_2 \longrightarrow R_3SbCl_2 + CO_2 \qquad (54)$$

Stibine dichlorides prepared in this manner are much purer than products obtained by direct chlorination of triaryl stibines. It should be mentioned that phosphine oxides also can be converted with phosgene to the corresponding dichlorides. An example is the reaction of triphenyl phosphine oxide:

$$Ph_3PO + OCCl_2 \longrightarrow Ph_3PCl_2 + CO_2 \qquad (55)$$

The triarylstibine imines, prepared according to Equation 53, are much less stable than the corresponding phosphine imines. Even at room temperature, all stibine imines slowly split off ammonia and form polymeric products. Over 60°C, ammonia is evolved very rapidly. Among the lower polymeric products, it was possible to isolate the substance $Ph_3Sb{=}N{-}SbPh_3{-}\bar{N}{=}SbPh_3$ (XI). Hydrogen cyanide and other nitriles accelerate the splitting off of ammonia. Compound XI is thereby formed as the main product, according to Equation 56.

$$3\,Ph_3SbNH \longrightarrow \underset{\text{XI}}{Ph_3Sb{=}\bar{N}{-}SbPh_3{-}\bar{N}{=}SbPh_3} + NH_3 \qquad (56)$$

Besides the great tendency of triarylstibine imines to split out ammonia and polymerize, they characteristically take part in the following three types of reactions:

1. As nitrogen bases
2. Substitution of the imino-hydrogen
3. Replacement of the NH-group by oxygen or sulfur

In its basic reactions, triphenylstibine imine acts as a secondary amine. With anhydrous hydrogen halides or with anhydrous formic acid, triphenylstibine-iminium salts form:

$$Ph_3Sb = NH + HX = (Ph_3SbNH_2)X;\ X = Cl',\ Br',\ J';\ HCOO' \qquad (57)$$

In contrast to triphenylstibine imine, triarylstibine imines with para substituents of the first order (i.e., ortho and para directing groups) behave differently, due to the influence of the phenyl substituent. With hydrogenhalides, iminium salts do not form; instead the reaction proceeds as in Equation 58.

$$R_3Sb{=}NH + 3HX = R_3SbX_2 + NH_4X \qquad (58)$$

$$X = Cl, Br;\quad R = -C_6H_4-CH_3,\ -C_6H_4-O-CH_3,\ -naphthyl$$

Among the reactions of triarylstibine imines involving substitution of the imino-hydrogen, there might be mentioned replacement by the tosyl group using p-toluenesulfonic acid: the corresponding N-tosyl imines are formed. Halogens react with triphenylstibine imine to yield the strongly-oxidizing N-halogen triphenylstibine imines, which are stable in solution for only a short time:

$$2\ Ph_3Sb = NH + Cl-SO_2-C_7H_7 = (Ph_3SbNH_2)Cl + Ph_3Sb=N-SO_2-C_7H_7 \qquad (59)$$

$$4(H_3C-Ph)_3Sb=NH + 3Cl-SO_2-C_7H_7 = 3(H_3C-Ph)_3Sb=N-SO_2-C_7H_7 + (H_3C-Ph)_3SbCl_2 + NH_4Cl \qquad (60)$$

$$Ph_3Sb=NH + X_2 \longrightarrow Ph_3Sb=N-X + (Ph_3SbNH_2)X;\ X = Cl,\ Br,\ J \qquad (61)$$

NH- oxygen and NH- sulfur replacements were observed in the reactions of triphenylstibine imines with oxygen and sulfur compounds.

Benzophenone is converted to diphenylketimine, which can be isolated as the hydrochloride:

$$Ph_3Sb=NH + O=CPh_2 \longrightarrow Ph_3Sb=O + NH=CPh_2 \xrightarrow{HCl} (Ph_2C=NH_2)Cl \qquad (62)$$

Phenyl isocyanate yields phenyl cyanamide:

$$Ph_3Sb=NH + Ph-N=C=O \longrightarrow Ph_3Sb=O + Ph-NH-CN \qquad (63)$$

Phenyl isothiocyanate also gives phenyl cyanamide:

$$Ph_3Sb=NH + Ph-N=C=S \longrightarrow Ph_3Sb=S + Ph-NH-CN \qquad (64)$$

In the reaction of triphenylstibine imine with acetyl chloride, triphenylstibine oxide and acetonitrile were formed, probably via an intramolecular NH - O exchange in the unstable intermediate, N-acetyl triphenylstibine imine:

$$2\,Ph_3Sb{=}NH + Cl-CO-CH_3 \longrightarrow Ph_3Sb{=}O + CH_3-CN + (Ph_3SbNH_2)Cl \qquad (65)$$

Elemental sulfur is converted to heptasulfur imide:

$$Ph_3Sb{=}NH + S_8 \rightarrow Ph_3Sb{=}S + S_7NH \qquad (66)$$

SECTION VII

EXPERIMENTAL

Preparation of Silver Cyanate from Potassium Cyanate and Silver Nitrate (Reference 4)

$$AgNO_3 + K(OCN) \longrightarrow AgNCO + KNO_3$$

In order to prepare $SO_2(NCO)_2$ under absolutely anhydrous conditions, the following method was developed for the preparation of dry silver cyanate.

A total of 81 gm pulverized potassium cyanate (Reference 5) are dissolved in 800 ml cold water and the solution filtered through a large porcelain filter. The insoluble, gray impurities in the raw K(OCN) remain behind on the filter.

A total of 169 gm silver nitrate are dissolved in 600 ml cold water and added dropwise very rapidly to the well-stirred K(OCN) solution. The silver cyanate immediately forms as a white precipitate and is separated by vacuum filtration. The water-insoluble compound (Reference 6) is washed 5 times with 100 ml portions of cold water, followed by an alcohol wash and finally with anhydrous ether to displace the alcohol. The precipitate is subsequently dried on an unglazed ceramic plate in the dark for three days at a pressure of 10 mm Hg.

The yield is practically quantitative; with the amounts used above (1 mole), this is about 150 gm AgNCO.

Preparation of Sulfuryl Diisocyanate, $SO_2(NCO)_2$, from Chlorosulfuryl Isocyanate and Silver Cyanate

$$ClSO_2 - NCO + AgNCO \longrightarrow SO_2(NCO)_2 + AgCl$$

In the search for the most economical method of preparing pure $SO_2(NCO)_2$, we developed the following procedure, which requires a minimum of AgNCO. In a 500 ml spherical flask with glass joint place 70 gm $ClSO_2NCO$ and 80 gm dry AgNCO; reflux with a 150° to 160°C oil bath for 45 hours, taking care to exclude traces of moisture. Under these conditions, a liquid slowly distills from the paste and drips steadily back from the condenser into the reaction mixture, which gradually becomes light yellow. After 45 hours, the reaction flask is connected in series to two cold traps with wide-bore tubing. The traps should be connected in the reverse order, i.e., dip-tubes on the outlet sides. The second cold trap is connected to a vacuum pump able to draw 2 to 4 mm Hg. The traps are cooled with acetone/dry ice. Great care must be taken to ensure that the system is vacuum tight.

The liquid reaction product is slowly distilled from the paste by holding at a pressure of 2 to 4 mm Hg for 1/2 hour at room temperature, then gradually increasing the temperature (1/2 hour at 60°C, 1/2 hour at 120°C, and finally 1/2 hour at 185°C). Sulfuryl diisocyanate, contaminated with some $ClSO_2NCO$, freezes out in the cold trap as fine white needles.

Starting, as above, with 70 gm $ClSO_2NCO$, the yield after this first conversion is 62 gm. Chloride analysis of the product is 7.2 percent, coming from unconverted starting material.

In order to achieve a quantitative conversion, the 62 gm of raw product are reacted with an additional 15 gm AgNCO. This mixture, now a suspension rather than a paste, is again heated for 45 hours with an oil bath at 150 to 160°C, as already described. The liquid part of the mixture is again distilled into cold traps, as before, raising the temperature with an oil bath to 185°C. Yield is 60.5 gm, with a chloride content of 0.5 percent.

To remove the last traces of chlorine, the reaction is once more repeated with an additional 15 gm AgNCO.

The final yield of chlorine-free sulfuryl diisocyanate is 58.3 gm; based on $ClSO_2NCO$, this is 80 percent of the theoretical amount. Considering the losses incurred in the distillations, the yield based on $ClSO_2NCO$ can be considered quantitative. Taking care to exclude traces of moisture from the air, the sulfuryl diisocyanate is distilled into ampules, which are then melted closed. The normal boiling point is 139°C.

Density of Sulfuryl Diisocyanate

For determination of the density of sulfuryl diisocyanate, 5-ml flasks were used, which had previously been calibrated with mercury. The liquid was slowly distilled into the flasks, avoiding contact with moisture. A constant temperature was provided by a thermostated bath at 22°C. The measuring flasks were very carefully sealed by melting above the calibration mark. Weighing by difference, the following results were obtained:

5 ml product (22°C) weigh 1) 7.9492 gm; d = 1.5898 gm/cm^3

2) 7.9268 gm; d = 1.5854 gm/cm^3

Average density at 22°C = 1.588 gm/cm^3

Reaction of Potassium Cyanate with Sulfur Trioxide

$$2\,K(OCN) + 4\,SO_3 \longrightarrow K_2S_2O_7 + S_2O_5(NCO)_2$$

$$S_2O_5(NCO)_2 \longrightarrow SO_2(NCO)_2 + SO_3$$

Upon careful distillation of dry sulfur trioxide onto potassium cyanate, the reaction mixture becomes liquid. Removal of excess sulfur trioxide causes resolidification; the product has the approximate composition $KOCN \cdot 2\,SO_3$. From this mixture, disulfuryl isocyanate can be sublimed in the form of large needles by heating in vacuum (MP 26°C). $S_2O_5(NCO)_2$ presumably forms according to the following mechanism:

$$K\left[\begin{array}{c|c} O & O \\ \hline OSO & SNCO \\ \hline O & O \end{array}\right]\left[\begin{array}{c|c} O & O \\ \hline OCNSO & SO \\ \hline O & O \end{array}\right]K \longrightarrow K_2S_2O_7 + S_2O_5(NCO)_2$$

Heating $S_2O_5(NCO)_2$ to 140°C causes decomposition to SO_3 and $SO_2(NCO)_2$.

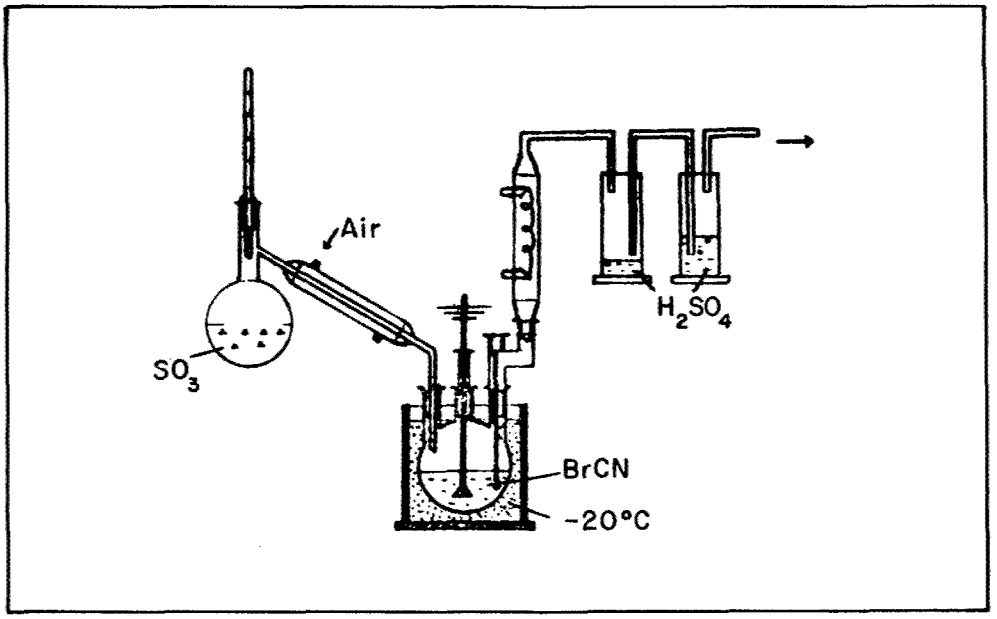
Reaction of Cyanogen Bromide with Sulfur Trioxide

The original patented process (Reference 7):

$$2\,BrCN + 3SO_3 \longrightarrow OCN\text{-}SO_2\text{-}O\text{-}SO_2\text{-}NCO + Br_2 + SO_2$$

$$OCN\text{-}SO_2\text{-}O\text{-}SO_2\text{-}NCO \longrightarrow SO_2(NCO)_2 + SO_3$$

A total of 424 gm of cyanogen bromide, which has been twice distilled over calcium chloride (Reference 8) is placed in a 1-liter, 3-neck flask, and cooled with a bath at -20°C. With good stirring, 480 gm SO_3 is slowly distilled into the flask. An exothermic reaction takes place, and the reaction mixture becomes fluid, with the formation of bromine and sulfur dioxide.



A reflux condenser prevents loss of cyanogen bromide. Two wash bottles with concentrated sulfuric acid protect the apparatus from moisture.

After completion of reaction, most of the bromine is removed by distilling at 20 mmHg; the bath temperature, however, must not exceed 50°C. The distillate receiver should be held at -20°C. If a water pump is used to create the vacuum, a long calcium chloride tube and a water trap must be placed in the line between the distillation apparatus and the pump. After ten minutes at 50°C, most of the bromine has distilled over. If a fine precipitate forms upon cooling the residue, moisture has seeped into the apparatus; this precipitate should be filtered off under anhydrous conditions. It must not be confused with the crystals of $OCN\text{-}SO_2\text{-}O\text{-}SO_2\text{-}NCO$, which forms large, clear prisms.

The filtrate is now warmed in an oil bath 150° to 160°C in a flask provided with a long, air-cooled reflux condenser, whose outlet is connected to two wash bottles containing small amounts of sulfuric acid to protect the flask contents from moisture. Considerable amounts of bromine and sulfur trioxide boil off. After 2 to 4 hours, the reaction product is clear, but becomes cloudy upon cooling and turns yellow-red. After 15 to 20 hours of this pyrolysis, the liquid product is distilled through a 30 cm long Widmer column. Two fractions are obtained:

1. BP 46°C Sulfur Trioxide

2. BP 130° to 139°C Crude $SO_2(NCO)_2$

The second fraction, a yellowish-red mobile liquid, contains a thermally unstable impurity. Upon heating to 140°C, it decomposes to bromine and a yellow precipitate. The liquid is heated to boiling in a distillation apparatus, whereupon the clear liquid becomes cloudy (yellow precipitate) and bromine is evolved. After 24 hours, the mixture is distilled at atmospheric pressure.

The boiling point is then 135° to 139°C. The pyrolytic removal of bromine and subsequent distillation is repeated twice. One obtains, thereby, a water-white liquid with a normal boiling point of 139°C. Melting point is -5°C.

Yield of pure product from 424 gm BrCN is 240 gm $SO_2(NCO)_2$, 81 percent of theory.

Reaction of Sulfuryl Diisocyanate

A. Complete Hydrolysis

$$SO_2(NCO)_2 + 2\,HOH \longrightarrow SO_2(NH_2)_2 + 2\,CO_2$$

Into an 800 ml Erlenmeyer flask containing a 1 cm deep layer of water, a definite amount of $SO_2(NCO)_2$ was added dropwise. A vigorous reaction ensued, with evolution of carbon dioxide, and formation of a clear solution. After the reaction had subsided, the solution was heated to boiling for 5 to 10 minutes, whereupon additional carbon dioxide evolved. Subsequently the water was removed at 60° to 70°C in vacuum. The dry residue dissolved completely in acetone, from which it precipitated upon evaporation. Melting point was 89°C. From the Debye-Scherrer diagram, the product could be identified as sulfamide.

B. Partial Hydrolysis of $SO_2(NCO)_2$ with One Mole Water

$$SO_2(NCO)_2 + 1\,HOH \longrightarrow H_2N-SO_2-NCO + CO_2$$

Due to the great reactivity of $SO_2(NCO)_2$, it is absolutely necessary that the reaction be carried out with exactly one mole water, and that there be no extraneous sources of moisture.

1. The apparatus must be dry. This can be achieved by assembling the parts hot after heating for one hour at 160° to 170°C in a drying oven, closing off the outlet with a large tube filled with phosphorus pentoxide, then letting cool to room temperature.

2. Solvent for the reaction is anhydrous acetonitrile, which has been distilled six times over phosphorus pentoxide into a receiver also containing phosphorus pentoxide. The solvent is then finally distilled a seventh time into a receiver dried in the manner described above. Even if one has worked very carefully under dry conditions, the acetonitrile generally still contains 0.02 percent water, which must be taken into account (water titration by Karl-Fischer).

3. No stirrer is used in order to avoid the chance of air entry through the rotating joint. Our experience shows it is best to add the required amount of water slowly to the reaction flask with shaking, and with occasional water cooling to keep the flask contents under 25°C.

Place 125 ml acetonitrile in a 500 ml, 2- or 3-neck flask and add 5.0 gm $SO_2(NCO)_2$. After mixing well, the partial hydrolysis can be carried out by slowly adding the required water. A special burette is needed, with 0.01 ml calibrations. If the acetonitrile still contains 0.02 percent water, a corresponding amount must be deducted from the calculated quantity of water to be added. The partial hydrolysis requires 0.58 ml (18°C) water. This should be added within 3 to 4 minutes. During the reaction, very little carbon dioxide is evolved through the P_4O_{10} drying tube. Assuming 100 percent yield, the flask should then contain 4.12 gm H_2NSO_2NCO.

All the experiments and reactions of amidosulfuric acid isocyanate described below were carried out using acetonitrile solutions of H_2NSO_2NCO prepared as just described.

Determination of Water in Acetonitrile by Karl-Fischer

(Factor 0.008 gm)

Sample, gm	I_2 Solution Used, ml	Water Content, %
6.3080	0.15	0.019
20.6153	0.45	0.018

The two samples came from different solutions.

Attempt to Isolate Monomeric Amidosulfuric Acid Isocyanate

A solution of H_2NSO_2NCO, freshly prepared by the partial hydrolysis of $SO_2(NCO)_2$ in acetonitrile, is immediately distilled in high vacuum (0.1 mm Hg) at a temperature of -5° to -10°C, taking great pains to maintain absolutely anhydrous conditions throughout. After about 5 minutes there is left in the flask an oily residue, which soon solidifies. This substance does not have a sharp melting point. It is somewhat soluble in water, giving a solution with a pH of 2. Concentrated aqueous solutions are viscous.

Analysis: Sulfate — negative; nitrogen-bonded sulfur (nitrite in acid solution) — positive; water solutions at room temperature evolve CO_2. Calculated for polymeric sulfuryl urea, $-(SO_2NH\text{-}CO\text{-}NH\text{-})_n$: C, 9.84; H, 1.64; N, 22.95; S, 26.25. Found: C, 11.17; H, 1.54; N, 23.49; S, 25.62.

Titration of the Protons formed in Polymerization of H_2NSO_2NCO

In a 500-ml spherical flask, 5.00 gm $SO_2(NCO)_2$ were dissolved in 125.0 ml acetonitrile (0.02% water) and partially hydrolyzed with 0.58 gm water. The solution was kept at a constant temperature of 25° ± 0.2°C with a large water bath. The flask was connected to a large drying tube filled with phosphorus pentoxide to prevent entrance of moisture.

Immediately following the partial hydrolysis, a 10-ml sample was removed with a vacuum pipette. At measured intervals, further 10-ml samples were similarly removed. The samples were quickly sprayed into 50.0 ml water at 25°C. Carbon dioxide evolved very rapidly; excess

CO_2 was removed by shaking. Temperature of the solutions was always kept at 26°C in this step. The solutions prepared in this manner were titrated with 0.01 n NaOH, against methyl orange as indicator. The endpoint in the first three titrations was not sharp. For the determination of the final value after completion of reaction (72 hours, 10 minutes), only 5 ml of solution were left. This was sprayed into 25 ml water (CO_2 evolution) and titrated; the titer was multiplied by 2. The results were:

Time, Min	Volume 0.01 n NaOH, ml
0	31.5)
30	45.9) Endpoint not sharp
90	53.8)
150	55.1
180	61.5
210	68.9
270	80.2
330	92.0
390	108.3
450	119.9
510	134.9
570	147.3
-	-
4330	ca 310

Identification of the Polymerization Products

Five grams $SO_2(NCO)_2$ were partially hydrolyzed to H_2NSO_2NCO, in the manner already described. At measured time intervals, samples were withdrawn from the solution and sprayed into a small amount of water to hydrolyze the remaining free isocyanate groups. After removing the water at 35° to 40°C in vacuum, determinations were made of the acid strength and melting point of the residue. In this product mixture, it was possible to observe microscopically the typical crystal form of urea disulfonamide (UDSA). The presence of UDSA was verified with a Debye-Scherrer diagram. The results of this study are:

Reaction Time, Min	pH	$SO_2(NH_2)_2$	UDSA	Polymeric Sulfuryl Urea
0	2-3	+ MP = 88°C	-	-
90	2	+ MP = 83-87°C	+ MP = 123°-137°C (small amt)	-
240	2	+ MP = ca 80°C	+ MP = 115°-120°C	+ somewhat gelatinous
ca 1500	2	-	-	+ gelatinous mass, totally amorphous

Ammonolysis of Amidosulfuric Acid Isocyanate in Acetonitrile - a New Method for Urea Monosulfonamide.

$$H_2NSO_2NCO + 2\,NH_3 \longrightarrow (H_2NSO_2-\underline{\bar{N}}-CO-NH_2)^- NH_4^+$$

Anhydrous gaseous ammonia (well dried) is passed into a solution of 4.12 gm H_2NSO_2NCO in 150 ml acetonitrile. After a few seconds, a precipitate begins to form. At completion of reaction (10 to 15 min), the precipitate is filtered off. The yield is 92 percent. The raw product has an unsharp melting point at 120°C. After twice recrystallizing out of water with alcohol, the salt melts sharply at 123°C. A mixture with the ammonium salt of urea monosulfonamide shows no melting point depression. Aqueous solutions have a pH of 6 to 7. Sulfate is absent. The test for nitrogen-bonded sulfur is positive. In the presence of strong caustic, ammonia is evolved.

Preparation of Amidosulfuryl Urethane

$$H_2NSO_2NCO + C_2H_5OH \longrightarrow H_2NSO_2NH-CO-OC_2H_5$$

A solution of 5.0 gm $SO_2(NCO)_2$ in 125 ml acetonitrile is partially hydrolyzed with water (1:1 mole ratio) to H_2NSO_2NCO, and 1.5 gm anhydrous ethyl alcohol is added. The reaction flask must be protected from moisture and the temperature must not exceed 25°C.

Since the reaction product is soluble in acetonitrile, the latter is removed in vacuum at 60°C. A residue of 5.5 gm, melting at 140°C, remains. The product can be recrystallized from water; upon slow evaporation of the water, the product precipitates as beautiful, large crystals up to 1.5 cm long. A further recrystallization from a small amount of ethyl acetate, in which the substance is quite soluble, gives an analytically-pure product. Needles, MP = 142.5°C; pH aqueous solution = 3. Aqueous solutions show no sulfate. Reaction with nitrite and $BaCl_2$ in HCl-solution is positive for the S-N bond.

Solubility

Water (cold)	very slightly soluble
Water (warm)	soluble
Methanol	soluble
Acetonitrile	soluble
Ethyl Acetate	soluble
Benzene	insoluble
Glacial Acetic Acid	soluble

Analysis: Calculated for $H_2NSO_2NHCO-OEt$: C, 21.44; H, 4.76; N, 16.67; S, 19.06; mol wt, 168. Found: C, 21.62; H, 4.97; N, 16.61; S, 1885; mol wt in glacial acetic acid, 149.

Reaction of Amidosulfuric Acid Isocyanate with 2,4-Dinitrophenyl Hydrazine to Form 1-(2,4-Dinitrophenyl)- 4-Amidosulfuryl Semicarbazide

$$H_2NSO_2NCO + H_2N\text{-}NH\text{-}C_6H_3(NO_2)_2 \longrightarrow H_2NSO_2NH\text{-}CO\text{-}NH\text{-}NH\text{-}C_6H_3(NO_2)_2$$

To a solution of 4.12 gm H_2NSO_2NCO in 200 ml acetonitrile, add 6.7 gm solid, well-dried 2,4-dinitrophenyl hydrazine. Temperature should be kept at 25°C. Moisture must be excluded. With shaking, the dinitrophenyl hydrazine slowly dissolves and after 1 to two minutes a yellow precipitate starts to form. Shaking is continued until the red color of dinitrophenyl hydrazine dissappears (ca 5 minutes). After 15 minutes, the flask is heated on reflux until the solid has almost completely dissolved (50 ml additional acetonitrile required). The insolubles are removed by filtration and the liquid slowly cooled to 0°C. Long (1.5 cm) silky yellow needles separate. The product is recrystallized from acetonitrile twice more. MP = 168°C (dec), needles turning cloudy at 120°C. The yield of raw product, after removing all but 50 ml of the solvent in vacuum at room temperature, is ca 9 gm. At room temperature, the product is only slightly soluble in water, giving a pH = 3. The aqueous solution shows no sulfate ion. The test for nitrogen-bonded sulfur is positive. Warm ammoniacal silver nitrate is reduced.

Both as crystals and in solution the substance shows a green fluorescence which, under an ultraviolet light, is strong enough to be observed even in strong daylight. Alkaline solutions are deep brown. This color change from light yellow to brown upon addition of a small amount of sodium hydroxide is clearly observable even in very dilute solutions. The brown alkaline solutions become light yellow again upon addition of acid. The product is hydrolyzed in boiling water. If a 5 to 10 percent solution is boiled 10 minutes, the light yellow solution turns an orange-red. Upon cooling, a small amount of yellow needles separates (MP = 168°C); also a red substance melting at 191°C. The latter shows no melting point depression with 2,4-dinitrophenyl hydrazine, and the Debye-Scherrer diagram is identical with that of dinitrophenyl hydrazine. Upon evaporating the water from the filtrate (66°C / 20 mm Hg), sulfamide could be recovered and identified by melting point (82°C) and Debye-Scherrer.

Analysis: Calculated for $H_2NSO_2NHCO\text{-}NHNHC_6H_3(NO_2)_2$ + 1 CH_3CN: C, 29.9; H, 3.05; N, 27.15; S, 8.9. Found: C, 29.87; H, 3.15; N, 26.87; S, 9.10.

The compound (MP 168°C) dissolves in hot dioxane. Upon cooling, a solid separates which, however, does not redissolve on reheating. It was filtered off and washed with ether. This yellow product now consists of prismatic crystals. Melting point is also sharp at 168°C.

Analysis: Calculated for $H_2NSO_2NHCO\text{-}NHNHC_6H_3(NO_2)_2$ + 1.5 Mol Dioxane: C, 34.5; H, 4.43; N, 18.6; S, 7.08. Found: C, 34.10; H, 5.25; N, 18.41; S, 7.14.

No appreciable amounts of dioxane could be removed at 100°C and 1 mm Hg pressure over phosphorus pentoxide for 20 hours. The nitrogen and sulfur analyses were then 18.33 percent and 7.22 percent, respectively. The needles containing one mole of acetonitrile could be freed of solvent by drying four days at 100°C and 4 mm Hg pressure.

Analysis: Calculated for $H_2NSO_2NHCO\text{-}NHNHC_6H_3(NO_2)_2$: C, 26.25; H, 2.5; N, 26.25; S, 10.0; mol wt, 320. Found: C, 26.46; H, 2.60; N, 26.34; S, 9.85; mol wt, cryoscopic in glacial acetic acid, 300.

Indicator Properties of the Semicarbazide

Measured amounts of hydrochloric acid, containing a few drops of a 1 percent alcoholic solution of the indicator, were titrated with standard NaOH. The color change from light yellow to brown was taken as the endpoint. The results are:

0.1 n HCl Used, ml	0.1 n NaOH Titer, ml
10.00	10.1
15.00	15.05
20.00	20.05
25.00	25.05

Measured amounts of NaOH, containing a few drops of a 1 percent alcoholic solution of the indicator, were titrated with standard HCl. The color change from brown to light yellow was taken as the endpoint. The results are:

0.1 n NaOH Used, ml	0.1 n HCl Titer, ml
10.00	9.95
15.00	15.00
20.00	19.95
25.00	25.0

The color change occurs at a pH of 4.6 ± 1; this indicator is, therefore, suitable for titrating urea disulfonamide, a compound prepared in the course of this work. The potentiometric titration of this compound shows a very sharp jump from pH 3.8 to pH 7.2, corresponding to the first dissociation. An actual test showed that this indicator was, indeed, satisfactory.

Reaction of Amidosulfuric Acid Isocyanate with Urea for the Preparation of Amidosulfuryl Biuret

$$H_2NSO_2NCO + CO(NH_2)_2 \longrightarrow H_2NSO_2NH-CO-NH-CO-NH_2$$

A fresh solution of 4.12 gm(max) H_2NSO_2NCO is prepared by the partial hydrolysis of $SO_2(NCO)_2$ in 150 ml acetonitrile. To this is added 2.03 gm solid, dry urea. With shaking, the urea completely dissolves at a temperature of 25°C. Precipitation begins in about one minute; after fifteen minutes, the solid is filtered off. Weight = 5.7 gm, MP = 143 to 1440°C (unsharp). Upon evaporation of the filtrate to dryness, 0.3 to 0.4 gm solid remain, having an unsharp melting point of 141°C. The two substances show the same Debye-Scherrer diagram.

After recrystallizing four times from hot water, the crystals melted sharply at 158°C. No CO_2 was evolved during the recrystallizations. The compound is only slightly soluble in cold water; concentrated solutions have a pH of 2. A test for sulfate ions with $BaCl_2$ was negative. The reaction with nitrate in HCl solution was positive.

Analysis: Calculated for Amidosulfuryl biuret: C, 13.2; H, 3.30; N, 30.8; S, 17.6. The sample was brought into solution by heating to 32°C; mol wt, 182. Found: C, 13.22; H, 3.54; N, 30.70; S, 17.65; mol wt, (cryoscopic in glacial acetic acid), 181.

Synthesis of Amidosulfuryl Thiobiuret from Amidosulfuric Acid Isocyanate and Thiourea

$$H_2NSO_2NCO + CS(NH_2)_2 \longrightarrow H_2NSO_2NH\text{-}CO\text{-}NH\text{-}CS\text{-}NH_2$$

To a solution of 4.12 gm H_2NSO_2NCO in 150 ml anhydrous acetonitrile are added 2.9 gm dry thiourea, avoiding all contact with moisture. At 25°C, the thiourea dissolves with shaking. After about one minute, precipitation begins. The solid is filtered off after 15 minutes. Yield: 5.6 gm. The filtrate contains about 1.4 gm more of product in solution. The precipitate dissolves in a 50 percent aqueous acetone solution, and recrystallizes again as the acetone slowly evaporates at room temperature. The very compact crystalline mass is thoroughly washed with ethyl acetate and dried over calcium chloride in a desiccator. The crystals melt sharply at 148°C, with decomposition. Aqueous solutions are strongly acid, pH = 2. Sulfate ions are not present. The test for nitrogen-bonded sulfur with nitrite in HCl solution is unusually strong.

Analysis: Calculated for Amidosulfuryl thiobiuret: C, 12.12; H, 3.06; N, 28.3; S, 32.35; mol wt, 198. Found: C, 12.71; H, 3.38; N, 28.24; S, 32.05; mol wt, cryoscopic in glacial acetic acid, 176.

Reaction of Amidosulfuric Acid Isocyanate with Sulfamide

$$2\,H_2NSO_2NCO + SO_2(NH_2)_2 \longrightarrow SO_2(NH\text{-}CO\text{-}NHSO_2NH_2)_2 \qquad \text{I}$$

$$H_2NSO_2NCO + SO_2(NH_2)_2 \longrightarrow H_2NSO_2NH\text{-}CO\text{-}NHSO_2NH_2 \qquad \text{II}$$

A. Experiment 1: Preparation of Sulfuryldi- (urea Sulfurylamide) (I)

Five grams of $SO_2(NCO)_2$ in 125 ml acetonitrile were partially hydrolyzed to H_2NSO_2NCO. Under absolutely anhydrous conditions, a solution of 3.24 gm $SO_2(NH_2)_2$ in acetonitrile was added from a dropping funnel, maintaining a temperature of not over 25°C. After about 20 seconds, with slow dripwise addition of the sulfamide solution, precipitation started. After 15 to 20 minutes, the precipitate was filtered off. Yield: 5.5 gm; MP = 160-170°C. The product was only slightly soluble in cold water, but quite soluble in hot water, with evolution of carbon dioxide. Concentrated aqueous solution had a pH of 2. A Debye-Scherrer analysis showed that sulfuryl di-(urea sulfuryl amide) had formed.

A solid residue could be recovered from the filtrate by removal of the solvent. MP = 87°C, ca 1.7 gm. This material was identified as sulfamide by its Debye-Scherrer diagram.

B. Experiment 2: Preparation and Hydrolysis of Sulfuryldiurea Sulfurylamide (I)

In this experiment, the order of addition was the reverse of that used in Experiment 1. Under anhydrous conditions, a solution of 4.12 gm H_2NSO_2NCO in 125 ml acetonitrile was added dropwise to a solution of 3.24 gm sulfamide in 80 ml acetonitrile. After 15 minutes, the resulting precipitate was filtered off. Yield: 5.9 gm. MP = 160°C (not sharp). The products of Experiments 1 and 2 were identical in their properties and in their Debye-Sherrer diagram.

After evaporating the filtrate, 1.3 to 1.4 gm of sulfamide were recovered, as in Experiment 1. MP = 87°C.

Recrystallizing the products from both experiments three times from hot water resulted in evolution of carbon dioxide and the formation of urea disulfonamide as beautiful crystalline plates melting at 152°C. Identification was by Debye-Scherrer.

Preparation of Urea Disulfonamide (II)

The best, and most direct, synthesis of urea disulfonamide (UDSA) is by the hydrolysis of $SO_2(NCO)_2$ according to:

$$2\,SO_2(NCO)_2 + 3\,H_2O \longrightarrow H_2NSO_2NH\text{-}CO\text{-}NHSO_2NH_2 + 3\,CO_2$$

Twenty-five grams $SO_2(NCO)_2$ are dissolved in 250 ml acetonitrile, which contains 0.02 percent water. With shaking and ice-cooling, 4.49 gm water are added dropwise form a burette calibrated in 0.01 ml divisions. After addition of 3.03 gm (0.6 mole) water, a precipitate forms and increases in quantity as more water is added. The precipitate is allowed to stand 15 minutes at room temperature, then filtered. Yield: 12.6 gm. Melting point of the raw product is 152°C. The Debye-Scherrer diagram shows that UDSA has formed. A residue of 6.0 gm sulfamide is recovered by evaporating the filtrate. MP = 87°C. The only slightly impure UDSA is carefully recrystallized once from water at 80°C.

Hydrolysis of Urea Disulfonamide

UDSA hydrolyzes in hot water, with evolution of carbon dioxide and the formation of sulfamide. Five minutes in water at 80°C suffices for a quantitative decomposition. No precipitate of UDSA forms upon cooling the solution. A 0.4977 gm sample of UDSA yielded:

1. CO_2 — qualitatively determined with $Ba(OH)_2$
2. Sulfamide — 0.4060 gm; MP = 89°C. Identification by Debye-Scherrer.
3. Amidosulfonic acid — 0.045 gm; MP 198°C. Identification by Debye-Scherrer.

To separate the hydrolytic products, the aqueous solution was evaporated to dryness at 40°C under vacuum. The dry residue was taken up in acetone; sulfamide dissolves, amidosulfonic acid does not.

In an exploratory experiment, sulfamide was boiled 5 minutes in 0.1 n HCl.

Products obtained:

Sulfamide	0.89 gm;	MP = 89°C; pH 4
Amidosulfonic acid	0.10 gm;	MP = 195°C

The method of separation of these two substances has already been described.

Titration of UDSA

A. Potentiometric Titration (Kalomel/Glass Electrode) Sample of UDSA - 0.0704 gm in 75 ml water at 25°C Titrant - 0.1 n NaOH, from a burette calibrated in 0.01 ml divisions

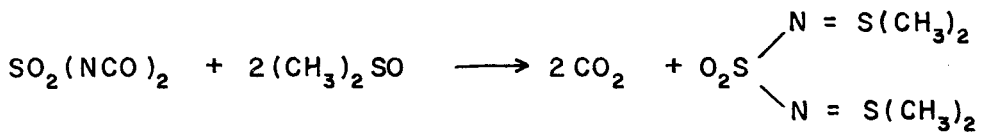
ml	pH	ml	pH	ml	pH	ml	pH
0	2.54	1.0	2.67	2.2	3.23	3.4	6.65
0.05	2.56	1.1	2.70	2.3	3.31	3.5	6.95
0.1	2.56	1.2	2.75	2.4	3.40	3.6	7.10
0.15	2.56	1.3	2.77	2.5	3.49	3.7	7.24
0.2	2.56	1.4	2.81	2.6	3.53	3.8	7.34
0.3	2.56	1.5	2.86	2.7	3.61	3.9	7.42
0.4	2.56	1.6	2.90	2.8	3.73	4.0	7.50
0.5	2.57	1.7	2.95	2.9	3.88	4.1	7.59
0.6	2.59	1.8	3.00	3.0	4.08	4.2	7.62
0.7	2.60	1.9	3.06	3.1	4.32	4.3	7.70
0.8	2.63	2.0	3.12	3.2	4.94	4.4	7.77
0.9	2.65	2.1	3.18	3.3	6.20	4.5	7.81
4.6	7.88	5.6	8.33	6.6	9.02	7.6	10.02
4.7	7.91	5.7	8.39	6.7	9.12	7.7	10.08
4.8	7.96	5.8	8.42	6.8	9.25	7.8	10.11
4.9	8.01	5.9	8.50	6.9	9.38	7.9	10.17
5.0	8.06	6.0	8.55	7.0	9.48	8.0	10.20
5.1	8.10	6.1	8.60	7.1	9.59		
5.2	8.15	6.2	8.69	7.2	9.70	8.5	10.30
5.3	8.20	6.3	8.78	7.3	9.79	9.0	10.37
5.4	8.25	6.4	8.83	7.4	9.89		
5.5	8.29	6.5	8.90	7.5	9.96		

B. Titration with 0.1 n NaOH Against Methyl Orange for the First Proton, and Against Thymolblue for the Second

Weight UDSA gm	0.1 n NaOH, ml (methyl orange)	0.1 n NaOH, ml (thymol blue)
0.0790	3.6	-
0.1659	7.4	-
0.1008	-	8.9
0.0910	-	8.15

Titration with phenolphthalein did not give a sharp endpoint, and the values were too low.

Reaction of Sulfuryl Diisocyanate with Dimethylsulfoxide



The reactants were combined in a mole ratio of 1:2. Since both NCO-groups in sulfuryl diisocyanate take part in the reaction, it was necessary to add the isocyanate dropwise to the dimethylsulfoxide, so that the latter was always in excess.

A solution of 0.2 mole dimethylsulfoxide in 50 ml absolute acetonitrile was placed in a well-dried 250 ml, 2-neck flask. To this was added dropwise from a dropping funnel, a solution of 0.1 mole sulfuryl diisocyanate in 50 ml absolute acetonitrile. An exothermic reaction set in immediately, with evolution of CO_2. When the addition was half complete, the solution became cloudy and a white crystalline substance precipitated. After the entire

solution had been added, the reaction mixture was boiled briefly and stirred overnight at room temperature. Subsequently, the precipitate was filtered off under anhydrous conditions, washed twice with acetonitrile and dried in vacuum. Yield: 11.8 gm. From the combined filtrate and washes, 2.5 gm additional product were recovered. The total yield, based on $SO_2(NCO)_2$, was 65 percent. After recrystallizing from acetonitrile three times, the sulfuryl bis-dimethylsulfimine melts at 177°C, with decomposition. In order to remove the exothermic heat of reaction, the reacting mixture was cooled with a water bath at 20°C. Stirring was accomplished with a glass-covered magnet.

The carbon dioxide evolved during reaction was allowed to escape through a wash bottle filled with concentrated sulfuric acid. The gas was absorbed in a saturated solution of barium hydroxide and determined as barium carbonate.

Analysis: Calculated for $C_4H_{12}N_2S_3O_2$: C, 22.2; H, 5.56; N, 12.96; S, 44.4. Found: C, 22.6; H, 5.54; N, 12.93; S, 45.3.

Chlorosulfuryl Isocyanate from Urea and Chlorosulfonic Acid

Starting materials: commercial urea; commercial chlorosulfonic acid, once distilled. For the preparation of larger quantities of chlorosulfuryl isocyanate, the method of Graf (Reference 3) was used.

Chlorosulfonic acid (267 gm) was added dropwise to 69 gm urea, with shaking and cooling. The reaction mixture was worked up by vacuum distillation. By fractional distillation of the volatile fraction frozen out in the cold trap, it was possible to obtain 14.3 gm of analytically pure product.

Analysis: Calculated for $CClNO_3S$: C, 8.48; Cl, 25.06; N, 9.89; S, 22.65. Found: C, 8.55; Cl, 25.81; N, 10.05; S, 22.88.

Fluorosulfuryl Isocyanate

$$FSO_3H + SO_2(NCO)_2 \longrightarrow FSO_2NCO + HOSO_2NCO$$

Sulfuryl diisocyanate (74 gm, 0.5 mole) was brought to the boiling point in a 2-neck flask provided with a dropping funnel and a take-off condenser. Keeping the mixture at the boiling point with an oil bath at 140° to 150°C, fluorosulfonic acid (50 gm, 0.5 mole) was added dropwise from the funnel. After each increment, the fluorosulfuryl isocyanate was allowed to distill from the mixture before adding more fluorosulfonic acid. The distillate receiver was cooled with ice-water. After three hours, addition was complete. The reaction flask contained a solid, white residue; 53 gm of a colorless liquid had distilled into the receiver. Yield: 85 percent. Boiling point of the raw product was 58° to 60°C.

Purification: The product contained some sulfur trioxide as impurity. This could be separated with an 80 cm long fractionating column, using a reflux ratio of 50:1. After fractionation, the FSO_2NCO boiled at 61.5°C.

Analysis: Calculated for $CFNO_3S$: C, 9.6; N, 11.2; S, 25.6; mol wt, 125. Found: C, 9.7; N, 11.1; S, 25.6; mol wt, cryoscopic in benzene, 113 (average).

Preparation of Imido bis-Sulfuric Acid Chloride from Chlorosulfuryl Isocyanate and Chlorosulfonic Acid

$$\underset{\text{I}}{Cl-SO_2-NCO} + \underset{\text{II}}{Cl-SO_2-OH} \longrightarrow \underset{\text{III}}{HN(SO_2Cl)_2} + CO_2$$

In a one-liter, 2-neck flask, provided with reflux condenser, thermometer, and gas outlet tube, a mixture of 166 gm I and 202 gm II is brought to a mild boil, using an oil bath at 160°C. In order to follow the course of reaction by means of the evolved carbon dioxide, the gas outlet tube is connected to a wash bottle filled with barium hydroxide. The evolution of carbon dioxide is slow and takes many hours. Reaction may be considered complete when the reflux temperature falls from its high of 140°C. Carbon dioxide evolution must also be complete. The reaction flask then contains rather pure imido-bis-sulfuric acid chloride, which solidifies in a cold bath at -30°C. The raw product is distilled in vacuum, BP=107° to 108°C (2 to 3 mm Hg). Yield: 214 gm (70% of theoretical). The substance is identical to that prepared by alternate routes.

The thermal instability of III is worth mentioning. Unlike imido bis-sulfuric acid fluoride, which distills at atmospheric pressure without decomposition, the chloride decomposes completely when boiled at normal pressure. During the decomposition, luminous blue flames can be seen on the surface, accompanied by the ordor of sulfur dichloride.

Preparation of Imido bis-Sulfuric Acid Chloride from Urea and Chlorosulfonic Acid

$$H_2N-CO-NH_2 + 3Cl-SO_2OH \longrightarrow \underset{\text{III}}{HN(SO_2Cl)_2} + NH_4HSO_4 + HCl + CO_2$$

Three moles (348 gm) chlorosulfonic acid are added dropwise to one mole (60 gm) urea, with cooling. The resulting solution is colored green by traces of chlorine. After a time, a colorless solid separates. The reaction mixture, without prior separation of the solid, is then distilled at a pressure of 1 to 2 mm Hg. Wide-bore apparatus must be used in this step to accommodate the stormy evolution of CO_2 and HCl. The solid residue (138 gm) consists of the ammonium salts of sulfuric acid, chlorosulfonic acid, and amidosulfonic acid. The distillate contains, besides imido bis-sulfuric acid chloride, primarily sulfuryl chloride, disulfuryl chloride, and chlorosulfonic acid. To purify further, the distillate is fractionate under vacuum. The more volatile components can be frozen out with liquid air. One obtains 78 gm of distillate, which is free of sulfuryl chloride but still contains large quantities of chlorosulfonic acid and disulfuryl chloride. The distillates from three runs are combined and fractionated again. The first fractions contain the disulfuryl chloride and chlorosulfonic acid. The product III then distills at 115°C/4 mm Hg; 14 gm. From the more volatile fractions in the cold traps, one can recover another 13 gm product. The yield based on urea is 4 percent. Melting point is 37°C.

Analysis: Calculated for $HNO_4S_2Cl_2$: H, 0.47; N, 6.54; S, 29.95; Cl, 33.12; mol wt, 214. Found: H, 0.85; N, 6.34; S, 29.7; Cl, 33.1; mol wt, cryoscopic in benzene 210.

Preparation of Imido bis-Sulfuric Acid Chloride from Phosphorus Pentachloride, Amidosulfonic Acid, and Chlorosulfonic Acid

$$2\,PCl_5 + NH_2\text{-}SO_2\text{-}OH \longrightarrow Cl_3P{=}N\text{-}SO_2Cl + POCl_3 + 3HCl$$

$$Cl_3P{=}N\text{-}SO_2Cl + ClSO_2OH \longrightarrow \underset{\text{III}}{HN(SO_2Cl)_2} + POCl_3$$

Dry amidosulfonic acid and dry PCl_5 are mixed in a mole ratio of 1:2 in a reaction flask provided with reflux condenser and drying tube. The mixture is then heated on a boiling water bath. After about 20 minutes, evolution of HCl begins; after 35 minutes, the mixture is fluid. Gas evolution continues for about 45 minutes, after which the $POCl_3$ is distilled out under a pressure of 20 mm Hg, using a bath temperature of 80°C. The residual oil, consiting mainly of trichloro-phosphazo sulfuric acid chloride, is mixed with technical chlorosulfonic acid in mole ratio of about 1:1.

The reaction flask is provided with a capillary for the introduction of dry nitrogen. The reflux condenser is connected via a drying tube to a water pump. Under vacuum, nitrogen is slowly pulled through the flask while it is heated for 8 hours at 80°C. Subsequently, unreacted chlorosulfonic acid is removed under vacuum. The bath temperature is thereby raised to 120°C. Finally, the product (III) is distilled at a pressure of 0.03 mm Hg, with a bath temperature of 80° to 120°C. Yield: ca 80 percent. MP=37°C. BP=114°C/4 mm Hg; 55°C/0.03 mm Hg $n_D^{25} = 1.4948$.

Analysis: Calculated for $HNO_4S_2Cl_2$: H, 0.47; N, 6.54; S, 29.95; Cl, 33.12; mol wt, 214. Found: H, 0.6; N, 6.56; S, 30.1; Cl, 33.4; mol wt cryoscopic in benzene, 210.

Preparation of Imido bis-Sulfuric Acid Fluoride from Fluorosulfuryl Isocyanate and Fluorosulfonic Acid

$$FSO_2NCO + FSO_2OH \longrightarrow HN(SO_2F)_2 + CO_2$$

One tenth mole (12.5 gm) fluorosulfuryl isocyanate and 0.1 mole (10 gm) fluorosulfonic acid are refluxed together in a 50 ml flask provided with a reflux condenser, whose outlet is closed off to entrance of moisture through a sulfuric acid wash bottle. The mixture is refluxed until evolution of CO_2 ceases. In order to avoid excessive separation of the reacting components due to the large differences in boiling points, the reaction was carried out at a moderate temperature, with the oil bath at 120°C; in addition, the flask was half-filled with glass Raschig rings. Evolution of carbon dioxide was finished after 150 hours. The imido bis-sulfuric acid fluoride was then distilled from the reaction flask under vacuum. Yield: 14.1 gm = 78 percent. BP=91°C/1 mm Hg; 173°C/765 mm Hg.

The chemical and physical properties of this product are identical to those of the imido bis-sulfuric acid fluoride prepared by the following method.

Preparation of Imido bis-Sulfuric Acid Fluoride from Urea and Fluorosulfonic Acid

$$H_2N\text{-}CO\text{-}NH_2 + 3FSO_2OH \longrightarrow HN(SO_2F)_2 + NH_4HSO_4 + HF + CO_2$$

A one-liter, 2-neck flask, provided with a drying tube and a dropping funnel, serves as a reaction vessel. The outlet of the dropping funnel is also provided with a drying tube. Sixty grams urea are placed in the flask. Since a reactant mole ratio of 1:3 is required, 300 gm pure fluorosulfonic acid is added dropwise from the funnel, and at such a rate that the reaction does not become too vigorous. Occasional immersion of the flask in a cold bath serves to remove the heat of reaction.

When all the fluorosulfonic acid has been added, the solution is slightly cloudy. After considerable time, a white precipitate settles out. If the reaction mixture is then distilled at a pressure of 2 to 0.1 mm Hg, a vigorous evolution of CO_2 and HF sets in. The distillate is a mixture of fluorosulfonic acid and a substance which crystallizes out at low temperatures. Separation of the two components was possible only with an efficient distillation column (Normag) at a reflux ratio of 50:1. A colorless, mobile liquid is thereby obtained.

From a series of reactions involving a total of 1198.9 gm fluorosulfonic acid, 853.1 gm were used up and 345.8 gm could be recovered. The weight of pure product obtained was 315.2 gm. MP=17°C. BP=170°C/760 mm Hg.

Reaction of Sulfuryl Diisocyanate with Ethylene Glycol

$$SO_2(NCO)_2 + HOCH_2CH_2OH \longrightarrow -(SO_2NH\text{-}CO\text{-}OCH_2CH_2\text{-}O\text{-}CO\text{-}NH-)_n$$

Sulfuryl diisocyanate (5 gm) is dissolved in 100 ml of benzene which has been dried over sodium. Under absolutely anhydrous conditions, 10 ml dry ethylene glycol is added dropwise to the stirred isocyanate solution. A gelatinous, greasy substance precipitates immediately. Solvent can be removed from the product by decantation and the polymer washed with acetone. For purification, the substance can be dissolved in dimethylformamide, a good solvent for this polymer. At high concentrations, the solutions are quite viscous. Addition of water or acetone causes reprecipitation.

Polymer purified in this manner was analyzed: Calculated for endless polymer chains: C, 22.9; H, 2.88; N, 13.35; S, 15.25. Found: C, 23.56; H, 3.58; N, 11.77; S, 13.90.

Assuming the chains are short and terminated with ethylene glycol molecules, the C and H values would be higher, and the N and S values lower than those calculated for endless chains.

$$HOCH_2CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{-}(SO_2\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_2CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH-)_n\ SO_2NH\overset{O}{\overset{\|}{C}}\text{-}OCH_2CH_2OH$$

For n = 3, the calculated analysis is: C, 23.9; H, 3.36; N, 12.4; S, 14.2.

The polymeric product melts sharply at 169°C with decomposition. The test for nitrogen-bonded sulfur, although slow, is clearly positive. Polysulfuryl-urethane is a granular, horn-like substance, which continues to burn when ignited in air, with the odor of burnt wool.

Solubility tests show the following:

Benzene	some swelling
Acetone	insoluble
Alcohol	insoluble
Acetonitrile	insoluble
Nitrobenzol	insoluble
Water	insoluble cold; very slightly soluble hot
Dimethylformamide	very soluble, giving highly viscous solutions

Reaction of Sulfuryl Diisocyanate with Ethylene Diamine

$$SO_2(NCO)_2 + H_2N\text{-}CH_2CH_2\text{-}NH_2 \longrightarrow -(SO_2NH\text{-}CO\text{-}NHCH_2CH_2NH\text{-}CONH-)_n$$

To a stirred, ca 10 percent solution of $SO_2(NCO)_2$ in anhydrous benzene (dried over sodium wire) at room temperature, add a ca 10 percent solution of anhydrous ethylene diamine in benzene. The apparatus is provided with a drying tube to exclude moisture.

Heat of reaction is easily removed by occasionally dipping the vessel in ice water. A white, solid mass immediately precipitates. There is no noticeable swelling of the product in benzene. In order to avoid an excess of ethylene diamine, the endpoint of the reaction was determined by testing a drop of the solution: evolution of CO_2 upon addition of water shows that the reaction is not yet complete. Evolution of heat of reaction also is an aid in determining the endpoint.

For purification, the product was dissolved in water, from which it could again be precipitated by addition of acetone in the form of a milky suspension which did not filter well, but from which the solid separated after 24 hours, permitting simple decantation of the solvent. The granular powder was dried in a desiccator over phosphorus pentoxide at a pressure of 20 mm Hg, after which it was thoroughly washed with acetone.

Aqueous solutions of this hydrophilic product show no primary sulfate. At elevated temperatures, the test for nitrogen-bonded sulfur is positive. The product is neutral. Upon heating, the substance swells at 120°C, then melts rather indefinitely at about 160°C.

At high temperatures, the substance decomposes with separation of carbon and is inflammable. The usual method for nitrogen determination with metallic sodium gave a positive test.

Reaction of Sulfuryl Diisocyanate with Anhydrous Hydrazine

$$SO_2(NCO)_2 + 2N_2H_4 \longrightarrow \underset{I}{-(SO_2N\text{-}CO\text{-}NHNH\text{-}CO\text{-}NH-)_n^{n-}(N_2H_3)_n^{n+}}$$

A. Experiment 1

Sulfuryl diisocyanate (7.4 gm) dissolved in a small amount of anhydrous acetonitrile is added dropwise to a solution of 3.2 gm hydrazine in acetonitrile, care being taken to exclude moisture. The reaction temperature should not exceed 25°C. A precipitate forms which is filtered off after 10 minutes. Yield: 9.6 gm. MP = 135° to 140°C (dec). Recrystallization out of water gives an oil that solidifies when dried in a desiccator over phosphorus pentoxide at a pressure of 15 mm Hg. X-ray analysis of this glassy substance reveals no lines. The melting point is sharp at 154°C (dec).

The product is soluble in water, giving a pH of 4. Concentrated solutions are viscous. Test for sulfate ions is negative. With nitrite in HCl solution, nitrogen-bonded sulfur is detectable. Cold, ammoniacal silver nitrate is strongly reduced. Addition of benzaldehyde to an aqueous solution results in the separation of benzalazine, which can be identified by melting point and mixed melting point with an authentic sample.

B. Experiment 2

If Experiment 1 is repeated with reversed order of addition (hydrazine added to the sulfuryl diisocyanate), the same product forms. Therefore, the order of addition has no effect on the course of the reaction.

Analysis of the product melting at 154°C: Calculated for I: C, 11.3; H, 3.8; N, 39.6; S, 15.1. Found: C, 11.35; H, 4.02; N, 38.08; S, 14.40.

Reaction of Phosphorus Pentachloride with Hydroxylamine in the Presence of Triphenylphosphine

A 500 ml, 3-neck flask was provided with a stirrer, reflux condenser (with drying tube), and gas inlet tube for nitrogen. The reagents were added to the flask in the following order: 20.6 gm (0.1 mole) PCl_5, 26.2 gm (0.1 mole) triphenylphosphine, 6.9 gm (0.1 mole) hydroxylammonium chloride, and about 200 ml pure tetrachloroethane. Subsequently, the mixture was vigorously stirred and heated under nitrogen for 3 hours at 130° to 140°C. After cooling, the solution was filtered under anhydrous conditions. Solvent was removed from the filtrate in a rotary evaporator, leaving a dark colored oil as residue, which was taken up in ether and allowed to stand for several days until the product crystallized out. The crystalline product was pressed on an unglazed ceramic plate and dried in a vacuum desiccator over paraffin.

Another recrystallization from acetonitrile gave 5 to 10 gm triphenylphosphine imine dichlorophosphate, melting at 186°C and giving no melting point depression when mixed with the product obtained in the reaction of N-bromo-triphenylphosphine imine and PCl_3. The infrared spectrum and Debye-Scherrer diagram of the product were identical with those of the authentic sample.

Analysis Phosphorus determination - as $MgNH_4PO_4 \cdot 6\ H_2O$, after oxidation in Parr bomb: Calculated for $C_{18}H_{15}NOP_2Cl_2$: P, 15.71. Found: P, 15.7.

Isolation of the Compound $(Ph_3P\text{-}\underline{\bar{N}}\text{-}PPh_3)^+(Cl_2OP\text{-}\underline{\bar{N}}\text{-}POCl_2)^-$ (I)

To isolate the compound I, the reaction between PCl_5, hydroxylamine, and triphenylphosphine, as described above, was repeated. However, the work-up procedure was modified. After filtering off the small amount of insolubles (1.3 gm) from the reaction mixture, the yellow-brown filtrate was concentrated by removing a large part of the solvent in a rotary evaporator. The residue was taken up in 15 ml cold acetonitrile, whereupon 6 to 7 gm of the already-described triphenylphosphine-imine dichlorophosphate precipitated. This was filtered off and washed with ether; after one recrystallization out of about 40 ml acetonitrile, the melting point was 180° to 186°C. A mixed melting point determination with the product obtained in the reaction described in the previous section showed no depression.

After removal of the precipitate, ether was added to the filtrate until crystals separated. Twelve hours were allowed for complete crystallization before filtering, followed by benzene and ether washes. Yield: 9.6 gm; MP = 161-65°C. The product could be purified by precipitation from acetone/ether. The melting point was then 166°C.

Analysis calculated for $C_{36}H_{30}N_2O_2P_4Cl_4$: C, 54.84; H, 3.83; N, 3.55; P, 15.71; Cl, 1798. Found: C, 55.12; H, 4.08; N, 3.29; P, 15.60; Cl, 17.80.

Preparation of Triphenylphosphine Imine

$$(C_6H_5)_3P + NH_2Cl \longrightarrow (C_6H_5)_3P\text{-}NH_2^+Cl^-$$

$$(C_6H_5)_3P\text{-}NH_2Cl + NaNH_2 \xrightarrow[liq\ NH_3]{} (C_6H_5)_3P\text{-}NH + NaCl + NH_3$$

In a 500 ml cold trap, which serves as a reaction vessel, 10 gm of triphenylphosphine are dissolved in 100 ml anhydrous ether and the vessel is connected in a stream of nitrogen to a chloramine generator. After connecting a second cold trap in series with the first, the two are cooled in a methanol-dry ice bath, and then chloramine generation is started, condensing the ammonia-chloramine mixture on to the ether-phosphine solution. The chloramine generator is shut off when 250 to 300 ml of the ammonia-chloramine has condensed in the two traps. Part of the product will already have crystallized. The contents of both traps are combined and the ammonia is allowed to evaporate through a drying tube filled with KOH. This is best accomplished by pulling the trap out of the cold bath until only about one third of the solution is in the cooling mixture. The turbulence caused by the boiling ammonia serves to mix the two phases. After complete evaporation of the ammonia and ether, 18 gm of a crystalline mixture of ammonium chloride and triphenylphosphine-iminium chloride remains. These are separated by extraction with ethyl acetate/methanol (9:1) in a Soxhlet; ammonium chloride is insoluble. Triphenylphosphine-iminium chloride is recovered from the extract by adding ether until precipitation is complete. After several recrystallizations from this solvent system, the melting point is 236°C. Yield is 10.5 gm, which is 80 percent, based on triphenylphosphine.

The deprotonation of triphenylphosphine-iminium chloride to triphenylphosphine-imine is carried out in a 750 ml, 3-neck flask. The two side necks are provided with gas inlet tubes for nitrogen and ammonia. The center neck is provided with a Y-joint, one side of which is connected to a mercury bubbler through which nitrogen can escape. The other side serves as an inlet for the solid reactant, which can thereby be added in a countercurrent stream of nitrogen, preventing access of moisture from the air.

Ammonia, which has been dried over quicklime, KOH, and sodium wire, is condensed into the flask (200 ml). In a countercurrent nitrogen stream, 722 mgm distilled sodium and a few crystals of iron nitrate are then added to the liquid ammonia. After a few hours, the blue

solution has become colorless, whereupon 12 gm of pulverized, well-dried triphenylphosphine-iminium chloride are added, the cold bath removed, and the ammonia allowed to distill out. When the ammonia has completely boiled off, the residue is dissolved in 300 ml anhydrous benzene and filtered under nitrogen to remove the insoluble sodium chloride and excess triphenylphosphine-iminium chloride. The benzene solution is concentrated down to a very small volume, causing precipitation of triphenylphosphine-imine in the form of colorless, plate-like crystals, which are filtered off under anhydrous conditions and dried in vacuum.

Recrystallization from cyclohexane yields 7.2 gm (83% of theory) pure triphenylphosphine-imine melting at 126°C.

Analysis: Calculated for $C_{18}H_{16}NP$: C, 77.96; H, 5.81; N, 5.05; P, 11.17; mol wt, 277.0. Found: C, 77.58; H, 5.94; N, 4.99; P, 11.15; mol wt, cryoscopic in benzene, 284.

N-Chloro Triphenylphosphine Imine

A solution of 27.7 gm (0.1 mole) triphenylphosphine imine in 350 ml absolute benzene is placed in a 500 ml, 3-neck flask, which is provided with a gas inlet tube and a drying tube. Chlorine for the reaction is first dried and then condensed into a small feed vessel from which it is evaporated and bubbled into the stirred reaction flask. The required amount for reaction is 3.55 gm (2.21 ml, 0.05 mole) which is added over a period of one-half hour, care being taken to avoid an excess.

During the period of chlorine addition, the solution becomes light yellow in color and colorless crystals of triphenylphosphine-iminium chloride start to separate. After reaction, these crystals are filtered off under anhydrous conditions and washed several times with absolute benzene. After recrystallization from a 9:1 mixture of ethyl acetate/methanol, the compound melts at 236°C and shows no melting point depression in mixture with an authentic sample of triphenylphosphine-iminium chloride. The benzene filtrate is concentrated in a rotary evaporator under vacuum; light yellow crystals of N-chloro triphenylphosphine imine separate. After subsequent recrystallization from a concentrated benzene solution, the product melts at 178° to 179°C.

In acid solution, this product oxidizes iodide quantitatively to iodine, a reaction which serves for its quantitative analysis. It is best to carry out the reaction in a mixture of acetonitrile, water, and dilute sulfuric acid, adding a weighed amount of N-chloro triphenylphosphine imine to this solution and titrating the iodine formed with thiosulfate, without the use of starch.

Yield of pure product is 8.9 gm (57% of theory).

Analysis calculated for $C_{18}H_{15}NPCl$: C, 69.34; H, 4.85; N, 4.49; P, 9.93; Cl, 11.37; mol wt, 311.73. Found: C, 69.73; H, 5.00; N, 4.75; P, 9.94; Cl, 11.20.

N-Bromo Triphenylphosphine Imine

A solution of 14 gm triphenylphosphine imine in 15 ml absolute benzene is placed in a 250 ml, 2-neck flask. With stirring, a solution of 4 gm bromine in 50 ml benzene is added dropwise over a period of 30 minutes. The solution becomes yellow in color and colorless crystals of triphenylphosphine-iminium bromide slowly start to separate. After 12 hours, the separation is complete and the crystals are filtered off under anhydrous conditions. Triphenylphosphine-iminium bromide melts, after recrystallization from acetonitrile, at 248°C. Yield: 8.1 gm.

Analysis calculated for $C_{18}H_{17}NPBr$: N, 3.91; Br, 22.32; mol wt, 358. Found: N, 3.92; Br, 22.51.

The yellow benzene filtrate is concentrated in a rotary evaporator under vacuum at room temperature, whereupon yellow crystals of N-bromo triphenylphosphine imine separate. After subsequent recrystallization from a concentrated benzene solution, the product melts at 170° to 172°C (not sharp). Yield: 8.6 gm, 92 percent of theory.

Analysis: Calculated for $C_{18}H_{15}NPBr$: C, 60.69; H, 4.24; N, 3.93; P, 8.69. Found: C, 60.54; H, 4.35; N, 4.20; P, 8.58.

Determination of oxidation equivalent: To an aqueous sulfuric acid solution in acetonitrile, containing an excess of KI, 190.1 mgm of the product is added and the iodine titrated with 0.1 n thiosulfate.

0.1 n thiosulfate used = 10.6 ml = 188.5 mgm N-bromo triphenylphosphine imine.

Molecular weight (cryoscopic in benzene) = 362.

N-Iodo Triphenylphosphine Imine

A solution of 27.7 gm (0.1 mole) triphenylphosphine imine in 200 ml absolute benzene is placed in a 500 ml, 3-neck flask. To this is added in the course of 1/2 hour a solution of 8.1 gm (0.05 mole) ICl in 100 ml absolute benzene, with stirring. An excess of the interhalogen must be avoided. The solution turns a deep orange-red and slightly yellow crystals of triphenylphosphine-iminium chloride start to separate. After completion of reaction, they are filtered off, washed with a small amount of absolute benzene. Following several recrystallizations from a 9:1 mixture of ethy acetate/methanol, the now colorless crystals melt at 236°C. Pure triphenylphosphine-iminium chloride can be obtained only after repeated recrystallizations. To save time, therefore, it is advisable to dissolve the raw product in water and convert it for purposes of identification with aqueous KI to the insoluble triphenylphosphine-iminium iodide. The triphenylphosphine-iminium iodide so formed can be recrystallized from hot water and then shows no melting point depression with an authentic sample of the iodide.

After removal of the triphenylphosphine-iminium chloride, the deep orange-red benzene filtrate is concentrated in a rotary evaporator under vacuum at room temperature, whereupon the orange-colored crystals of N-iodo triphenylphosphine imine separate. After subsequent recrystallization from about 30 ml benzene, the melting point is 174° to 175°C. As with all N-halogen compounds of triphenylphosphine imine, acid solutions of iodide are quantitatively oxidized to iodine, providing an analytical method for their determination. The procedure is exactly the same as already described for the N-chloro compound.

Yield of pure N-iodo triphenylphosphine imine: 8.6 gm = 43 percent of theory.

Analysis: Calculated for $C_{18}H_{15}NPI$: C, 53.61; H, 3.74; N, 3.47; P, 7.68; I, 31.47; mol wt 403.21. Found: C, 53.88; H, 3.87; N, 3.35; P, 7.69; I, 31.24.

Reaction of Triphenylphosphine-N-Bromimine with Trivalent Phosphorus Compounds

A. Reaction with Triphenylphosphine

$$Ph_3P{=}N{-}Br + Ph_3P \longrightarrow (Ph_3P{-}\underline{N}{-}PPh_3)\,Br$$

A solution of 2 gm triphenylphosphine in 50 ml benzene is added dropwise to a stirred solution of 1.1 gm triphenylphosphine-N-bromimine in 200 ml benzene. A light yellow oil separates, which crystallizes upon rubbing. After filtering, the product is dissolved in 150 ml hot water and allowed to crystallize by cooling. MP=256°C. Yield = 1.8 gm, 95 percent of theory. Bis-triphenylphosphine nitride bromide is soluble in many polar organic solvents.

Analysis: Calculated for: $C_{36}H_{30}P_2NBr$: C, 69.90; H, 4.88; N, 2.27; P, 10.01; Br, 12.93; mol wt, 618.2. Found: C, 69.61; H, 5.06; N, 2.23; P, 9.97; Br, 13.0.

Bis-triphenylphosphine nitride bromide is difficult to hydrolyze. The compound could be quantitatively recovered after boiling 3.97 gm for two hours in a mixture of 150 ml water and 50 ml concentrated HCl. In a boiling alkaline solution, on the other hand, the substance is slowly destroyed, forming triphenylphosphine oxide and ammonia. However, even after 24 hours boiling with 10 percent NaOH, the compound was only 50 percent hydrolyzed; the other half could be recovered unchanged.

B. Reaction with PCl_3

$$Ph_3P{=}N{-}Br + PCl_3 \xrightarrow[+\,HOH]{-\,HCl,\ -\,HBr} Ph_3P{=}N{-}\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{\overset{|}{\underset{|}{P}}}}{=}O$$

A solution of 2.45 gm (0.0177 mol) pure PCl_3 in 30 ml absolute benzene is placed in a 250 ml, one-neck flask provided with a magnetic stirrer and dropping funnel with pressure bypass. With vigorous stirring, a solution of 6.3 gm (0.0177 mole) N-bromo-triphenylphosphine imine in 150 ml absolute benzene is added dropwise over the course of one-half hour. A yellow oil starts to separate immediately, solidifying as the reaction proceeds. After complete addition of the imine, the light yellow product is filtered off under anhydrous conditions and washed a few times with absolute benzene. Yield: 8.6 gm. To avoid hydrolysis of this exceedingly sensitive substance, it is necessary to perform all operations under dry nitrogen.

To make the desired derivative of dichlorophosphoric acid, the salt-like compound formed in the first step is hydrolyzed under very mild conditions. This is accomplished by letting the compound stand in a flat, open vessel where it can be hydrolyzed by moisture in the air. HCl and HBr are evolved, leaving triphenylphosphine-imine dichlorophosphate. This hydrolysis may take 1 to 2 days. It can be accelerated, with some loss in yield, by a short digestion with a little ice-cold acetonitrile-water mixture. In this manner, 6.8 gm of an impure, more or less yellowish product are formed. Very pure product is obtained by recrystallizing this raw product twice out of 40 ml, then 25 ml acetonitrile. The product separates as magnificent colorless crystals. The substance melts at 186°C. Yield = 3.5 gm.

Reaction of Triphenyl Phosphite with Monochloramine

A solution of 2.59 gm (0.053 mole) monochloramine in 300 ml absolute ether was cooled to -45°C and added to a solution of 16.43 gm (0.053 mole) triphenyl phosphite in 100 ml absolute ether, also at -45°C. The reaction product immediately separated in the form of

colorless crystals. These were filtered off under anhydrous conditions, washed with ether and dried in vacuum. The yield of this quasi-phosphonium compound was 15.35 gm = 78.5 percent of theory, based on triphenyl phosphite used. The substance melted at 95° to 98°C. It contained about 3 percent ammonium chloride.

By concentrating the ethereal reaction solution, 2.01 gm diphenylamine phosphate precipitated (MP = 148-9°C; 15.2% of theory). Chlorobenzene could be identified in the remaining solution by means of gas chromatography.

Analysis: Calculated for

$$\left[(C_6H_5O)_3P(NH_2)\right]^+Cl^-$$

C, 59.7; H, 4.7; N, 3.8; P, 8.5; Cl, 9.7. Found: C, 58.7; H, 5.0; N, 3.6; P, 8.3; Cl, 10.0.

Analysis: Calculated for

$$(C_6H_5O)_2P(O)NH_2$$

C, 57.8; H, 4.8; N, 5.6; P, 12.4. Found: C, 58.0; H, 4.7; N, 5.6; P, 12.4.

Ammonolysis of the Quasi-Phosphonium Compound from Triphenyl Phosphite and Monochloramine

A total of 4.7 gm (0.013 mole) of the substance was suspended in 100 ml absolute ether. Anhydrous, gaseous ammonia was bubbled through this suspension for one hour. The resulting product was filtered off under anhydrous conditions. By distillation, 3.5 gm of phenol were recovered from filtrate. This is a yield of 95.6 percent. In addition, there was 0.6 gm of a product whose properties were identical to those of the product obtained by reacting triphenyl phosphite with an excess of ammonia and chloramine.

Reaction of Triphenyl Phosphite with Excess Monochloramine and Ammonia

A gaseous mixture of monochloramine-ammonia from the chloramine generator was passed for one hour into a solution of 10.05 gm (0.03 mole) triphenyl phosphite in 150 ml absolute carbon tetrachloride. The resulting precipitate was filtered off under anhydrous conditions on a porous glass filter and washed with three 100-ml portions of carbon tetrachloride in order to remove the phenol. After drying in vacuum from a water pump, there remained 4.1 gm dry product, equivalent to about 0.03 mole tetraaminophosphonium chloride. The reaction was quantitative.

Phenol was determined by first distilling off the carbon tetrachloride. The phenol residue was colored black by traces of indophenol. Subsequent distillation yielded 8.7 gm phenol (at 181°C and 760 mm Hg). This is 95.6 percent of theory.

An analysis of the tetraaminophosphonium chloride was carried out immediately after preparation to avoid loss of nitrogen through self-condensation of the product. The results were not completely satisfactory. Besides, the ca 5 percent ammonium chloride in the product could neither be removed nor separately determined. Its presence was reflected in analytical values.

Analysis: Calculated for

$$\left[(NH_2)_4P\right]^+ Cl^-$$

N, 42.9; P, 23.7; Cl, 27.1. Found: N, 41.7; P, 23.0; Cl, 28.5.

Preparation of Free Triarylstibine Imines from Triarylstibine Dichlorides

$$R_3SbX_2 + 2MeNH_2 \longrightarrow R_3Sb{=}NH + 2MeX + NH_3$$

X = Cl, Br, I
Me = Na, K

It is possible to obtain free triarylstibine imines in useful yields by means of the above reaction only if very pure reactants are used and all operations are carried out under absolutely anhydrous conditions. By the use of different halides and alkali metal amides, it was possible to vary the reaction velocity. The highest velocities were obtained by use of the dibromides and diiodides, especially when potassium amide was used, since the latter is very active and quite soluble in liquid ammonia.

For the preparation of pure potassium amide, free of hydroxide, ordinary commerical-grade potassium was distilled in high vacuum. Hydroxide-free potassium amide is generated directly in the reaction vessel. The dry potassium ampules are scratched in several places with a glass file and placed in the reaction bomb, which has been previously filled with dry nitrogen. There the ampules are smashed with a dry metal rod. After adding a trace of fused $FeCl_3$ as catalyst, the glass bomb is filled with anhydrous liquid ammonia (dried over sodium metal). When the blue potassium solution becomes colorless, the ammonia is allowed to condense back into the ammonia feed vessel and the calculated amount of anhydrous triphenylstibine dihalide is brought into the reactor. After cleaning the upper part of the bomb and filling with anhydrous liquid ammonia, the reaction tube was heated. Upon completion of reaction, the mixture was thoroughly extracted with tetrahydrofuran. For safety's sake, the reaction bomb must not be removed from the iron protective mantel during the course of reaction.

Preparation of Triphenylstibine Imine

Of the various combinations studied:

$$\phi_3SbCl_2/NaNH_2, \quad \phi_3SbBr_2/NaNH_2, \quad \phi_3SbI_2/NaNH_2,$$

$$\phi_3SbCl_2/KNH_2, \quad \phi_3SbBr_2/KNH_2,$$

the best proved to be ϕ_3SbBr_2/KNH_2.

In the reaction bomb, 2.07 gm hydroxide-free potassium amide (37.6 mmol) was prepared by reacting 1.47 gm pure, distilled potassium (37.6 mgm-atom) with anhydrous liquid ammonia. To this was added 8.36 gm anhydrous triphenylstibine dibromide (Reference 9) (16.3 mmol). After filling the bomb with 250 ml anhydrous liquid ammonia and completing the reaction, the reaction residue was extracted with three 170 ml portions of peroxide-free tetrahydrofuran.

The combined clear, yellow extracts were evaporated to dryness at room temperature in vacuum, taking care to exclude all moisture. After many hours drying in high vacuum, there remained 5.77 gm triphenylstibine imine (15.6 mmol) as a cream colored solid, corresponding to a yield of 96 percent of the theoretical weight. The product was free of halogen. It was stored under pure, dry nitrogen at -20°C.

Analysis: Calculated for N, 3.8; Sb, 33.08; mol wt, 368. Found: N, 3.57; Sb, 32.96; mol wt, cryoscopic in absolute dioxane, 340 (average).

Triphenylstibine imine does not possess a definite melting point. Upon heating to over 100°C, the substance sinters, decomposes, and turns dark, with the separation of metallic antimony.

Triphenylstibine imine is thermally unstable. Even at room temperature, as a solid or in solution, it slowly splits off ammonia. At temperatures over 65°C, this proceeds quite rapidly. The composition, therefore, steadily changes; for this reason, recrystallization from warm organic solvents is not possible.

Quite soluble with decomposition in acetone, methanol, ethanol, acetonitrile, nitrobenzene, ethyl acetate. Quite soluble without decomposition in absolute, peroxide-free tetrahydrofuran. Slightly soluble without decomposition in absolute dioxane. Very slightly soluble in absolute ether; benzene.

Triphenylstibine imine is extraordinarily sensitive to hydrolysis, yielding triphenylstibine oxide and ammonia, a property made use of in the Kjeldahl nitrogen determination. With absolutely anhydrous hydrogen halides or anhydrous formic acid, triphenylstibine imine forms thermally-stable iminium salts, which are, however, also hydrolytically unstable.

A trace of elemental sulfur added to a solution of triphenylstibine imine in absolute THF, ether, dioxane, or acetone causes dichroism: By reflected light, the solution is a deep, cornflower blue; by transmitted light, a ruby red. This color property provides a qualitative test for triphenylstibine imine: As little as 1 to 2 mg in 20 ml absolute THF is still detectable.

Preparation of Tris-(p-methyl phenyl)-Stibine Imine (Tris-p-tolyl Stibine Imine)

Of the combinations tried:

$$(H_3C-\phi)_3SbCl_2 / KNH_2, \text{ and } (H_3C-\phi)_3SbBr_2 / KNH_2 ,$$

the latter proved the better.

In the glass bomb reactor, 1.61 gm pure, distilled potassium (41.1 mgm-atom) was reacted with anhydrous liquid ammonia to give 2.26 gm hydroxide-free potassium amide (41.1 mmole). To this was added 10.10 gm absolutely dry tris-(p-methyl phenyl)-stibine dibromide (Reference 10) (18.1 mmole). The bomb was then filled with 250 ml absolute, liquid ammonia and kept at 40°C for 12 days, during which time a transitory red oil formed. After blowing off the ammonia, the residue was extracted with four, 180-ml portions of anhydrous, peroxide-free tetrahydrofuran. The combined extracts were evaporated to dryness at room temperature under vacuum, avoiding contact with moisture. A residue of 6.91 gm tris-(p-tolyl)-stibine imine (16.8 mmole) remained, corresponding to a yield of 93 percent of the theoretical weight. The product was free of halide. It was stored under dry, pure nitrogen.

Analysis: Calculated for N, 3.41; Sb, 29.68; mol wt, 410.15. Found: N, 3.23; Sb, 29.54; mol wt, cryoscopic in dioxane, 384 (average).

The THF-insoluble reaction residue was dissolved in hot water, acidified with 2 n HNO_3 and diluted to 500 ml. In a bromide determination (Volhard), a 10 ml aliquot of this solution required a titer of ϕ/7.15 ml 0.1 n $AgNO_3$, which represents 2.857 gm Br^- (17.87 mmol) in the total solution; that is, essentially all the bromide from $(H_3C\text{-}\phi)_3SbBr_2$ remains in the reaction bomb as THF-insoluble KBr.

The light yellow tris-(p-tolyl)-stibine imine had an unsharp melting point at 95° to 97°C (rapid heating); with slow heating, the product sintered. As solid or in solution, tris-(p-tolyl)-stibine imine continually releases ammonia, gradually changing in composition. Recrystallization from warm organic solvents is not possible.

Quite soluble, with decomposition, in acetone, methanol, ethanol, nitrobenzene, ethyl acetate. Quite soluble, without decomposition, in absolute, peroxide-free tetrahydrofuran. Slightly soluble, without decomposition, in absolute dioxane, benzene. Very slightly soluble, without decomposition, in absolute ether, petrol ether.

Tris-(p-tolyl)-stibine imine is extremely unstable hydrolytically, yielding tris-(p-tolyl)-stibine oxide and ammonia, a reaction which is made use of in the Kjeldahl nitrogen determination. With absolutely dry hydrogen halides, tris-(p-tolyl)-stibine imine forms the corresponding tris-(p-tolyl)-stibine dihalide, $(H_3C\text{-}\phi)_3SbX_2$, and ammonium halide.

Attempt at Preparation of Tris-(p-Methoxy Phenyl)-Stibine Imine

In the glass bomb reactor, 1.99 gm pure, distilled potassium (50.8 mgm-atom) was reacted with anhydrous liquid ammonia to give 2.80 gm hydroxide-free potassium amide (50.8 mmole). To this was added 7.82 gm dry tris-(p-methoxy phenyl)-stibine dichloride (15.2 mmole). After filling the bomb with 250 ml anhydrous liquid ammonia, the reaction was allowed to proceed at 40°C for 8 days. After 2 to 3 days, the ammonia solution was brown-black in color. The ammonia was subsequently allowed to evaporate and the residue thoroughly extracted with peroxide-free tetrahydrofuran. An insoluble residue remained in the bomb, consisting of excess potassium amide and potassium chloride. The combined, dark-brown THF extracts were free of halide.

After removing the solvent in vacuum at 0° to 5°C under anhydrous conditions, a resinous brown material remained, which could not be made to crystallize. It contained C, H, and Sb, but no nitrogen could be detected in the products of hydrolysis, nor by digestion with acids or bases. However, during removal of the THF solvent, large amounts of ammonia were evolved. That a free imine was present in the THF extract could be shown by the sulfur test reaction: 1 to 3 ml of the THF extract was added to 5 ml of a solution of sublimed sulfur in THF at a temperature of 0°C. The resulting solution was blue in reflected light and weakly ruby red in transmitted light. This test reaction was, however, positive only during the first hour after extraction of the reaction mixture with THF; after this time, it was negative. This indicates a complete decomposition of the unstable tris-(p-methoxy phenyl)-stibine imine, $(H_3C\text{-}O\text{-}\phi)_3Sb{=}NH$, which is initially present in the THF extract, but which decomposes fully during solvent removal. The imine could be determined qualitatively in the THF solution by hydrolysis, which yields ammonia and tris-(p-methoxy phenyl)-stibine oxide.

For this purpose, 30 ml water were added to 50 ml of the brown tetrahydrofuran extract; a colorless precipitate formed immediately. Since ammonia is continually evolved from the THF solution even prior to addition of water, it was not possible to distinguish the additional

ammonia evolved as a result of hydrolysis. The hydrolysis mixture was boiled for 10 minutes, then evaporated to dryness and the residue digested several times with alcohol at -20°C. The insoluble residue, after several recrystallizations from boiling, dilute alcohol, had a melting point of 191°C. It was identified as tris-(p-methoxy phenyl)-stibine oxide through mixed melting point and Debye Scherrer analysis. The insoluble reaction residue in the glass reaction bomb after THF extraction proved to be a mixture of excess potassium amide and potassium chloride.

Reaction of Phosgene with Triphenylphosphine Oxide and with Triphenylstibine Oxide

The reactions were carried out as follows, taking great pains to maintain absolutely anhydrous conditions at all times. The oxides were suspended or dissolved in absolute acetonitrile (the stibine oxide is only slightly soluble). Dry phosgene was then introduced at room temperature for 15 minutes, bubbling through the solution or passed across the surface. The solutions became slightly warm and turned yellow, with evolution of carbon dioxide. The latter could be determined qualitatively with $Ba(OH)_2$ without interference from phosgene by carrying the reaction out as follows: carefully add a saturated solution of phosgene in acetonitrile to a saturated solution of the oxide in such a way that the phosgene solution goes to the bottom; entrainment of phosgene is thereby avoided. After reaction, solvent was removed in vacuum at room temperature, and the products recrystallized from absolute solvents. The resulting dichlorides were identified by mixed melting points, Debye X-ray analysis, or by chemical analysis.

A. Reaction of Triphenylphosphine Oxide (Reference 11) with Phosgene

Weight $\phi_3P{=}O$: 9.75 gm (35.0 mmole) in 50 ml absolute acetonitrile.

Weight ϕ_3PCl_2 formed: 9.80 gm (29.4 mmole).

Yield of raw product = 84 percent of theoretical weight.

Purification: Reprecipitation from absolute benzene with absolute petrol ether. Melting point — indefinite.

Analysis: Calculated for: Cl, 21.3; P, 9.3. Found: Cl, 21.1; P, 9.11.

B. Reaction of Triphenylstibine Oxide (Reference 9) with Phosgene

Weight $\phi_3Sb{=}O$: 5.646 gm (15.3 mmole) in 50 ml absolute acetonitrile.

Weight ϕ_3SbCl_2 formed: 6.357 gm (14.9 mmole).

Yield of raw product: 98% of the theoretical weight.

Purification: Reprecipitation from absolute THF with absolute petrol ether. Melting point = 143°C.

Pyrolysis of Triphenylstibine Imine — Formation of N, N'-bis-(Triphenylstibino)-Triphenylstibine Diamine

$$3\,\phi_3Sb{=}NH \longrightarrow \phi_3Sb{=}N{-}Sb\phi_3{-}N{=}Sb\phi_3$$

In the glass bomb reactor, 1.36 gm pure, distilled potassium (34.7 mgm-atom) was reacted with liquid ammonia to give 1.91 gm hydroxide-free potassium amide (34.7 mmole). To this

was added 8.11 gm absolutely dry triphenylstibine dibromide (15.8 mmole). The bomb was then filled with 250 ml liquid ammonia and heated for 3 months at 45°C. After removal of the ammonia by evaporation, the residue was thoroughly extracted with peroxide-free tetrahydrofuran. The extracts were combined and evaporated to dryness in vacuum at room temperature under anhydrous conditions, leaving a residue of 5.49 gm of light yellow N, N'-bis-(triphenyl-stibino)-triphenylstibine diamine (5.0 mmole), corresponding to a yield of 96 percent of the theoretical weight. After repeated recrystallizations from a solvent mixture containing a small amount of THF in a large quantity of petrol ether, the melting point was 223°C. The product is extraordinarily sensitive to hydrolysis. It was stored under pure, dry nitrogen.

Analysis: Calculated for N, 2.57; Sb, 33.6; mol wt, 1087.19. Found: N, 2.46; Sb, 33.47; mol wt, cryoscopic in absolute benzene, 1055 (average). From these data, the atomic ratio of N to Sb = 1.00 to 1.58, which is very nearly 2 to 3; MP = 223°C.

Very soluble in absolute benzene, tetrahydrofuran. Very soluble, with decomposition, in absolute acetone, methanol, ethanol. Soluble in warm acetonitrile (suitable for recrystallization). Slightly soluble in petrol ether, CCl_4.

The substance is hydrolytically very unstable. With water or alkalis, hydrolysis yields triphenylstibine oxide and ammonia. With anhydrous hydrogen halides, the product splits into triphenylstibine dihalide, ϕ_3SbX_2, and triphenylstibine-iminium halide, $(\phi_3SbNH_2)X$. Unlike triphenylstibine imine, this product does not give a color reaction with elemental sulfur.

Reaction of Triphenylstibine Imine with p-Toluenesulfonyl Chloride

A solution of 3.27 gm triphenylstibine imine in 80 ml anhydrous, peroxide-free tetrahydrofuran was placed in a flask taking care to avoid contact with moisture. The imine had a nitrogen content of 3.58 percent, instead of the 3.80 percent in pure imine. The actual weight of triphenylstibine imine used was, therefore, 3.07 gm (8.3 mmole). A stoichiometric quantity of anhydrous p-toluenesulfonyl chloride (0.79 gm = 4.15 mmole), dissolved in 10 ml absolute benzene, was then added in a countercurrent stream of nitrogen. The reaction mixture was stirred three hours at room temperature, then warmed almost to boiling for 20 minutes. A colorless precipitate formed, which was filtered off under anhydrous conditions and recrystallized from hot acetonitrile. Melting point was 232°C (dec). The substance was identical to triphenylstibine-iminium chloride, as shown by mixed melting point, Debye X-ray, and Cl, N and Sb analyses. Yield = 1.12 gm = 2.7 mmole = 67 percent of the theoretical weight (a 100 percent yield would be 4.15 mmole). It would be expected that the filtrate should contain triphenylstibine-(N-p-toluenesulfonyl)-imine, $\phi_3Sb{=}N{-}SO_2{-}C_7H_7$, in the same yield.

After removing the iminium chloride, the filtrate was evaporated in vacuum to dryness, taking care to exclude moisture. Cyclohexane was added to the brown-yellow oily residue, causing separation of a flocculent white precipitate which was difficult to filter. Recrystallization from anhydrous benzene caused large losses, but gave 1.13 gm of colorless, needle-like crystals melting at 254° to 256°C (dec), which were identified as triphenylstibine-(N-p-toluenesulfonyl)-imine through mixed melting point, Debye X-ray and N, S, Sb analyses. (The chemical analyses were carried out after drying the product at 80°C in high vacuum.) An authentic sample for comparison was prepared by reacting triphenylstibine and anhydrous Chloramine-T (Reference 12).

Analysis: Calculated for N, 2.68; S, 6.13; Sb, 23.3. Found: N, 2.56; S, 5.99; Sb, 23.2.

Very soluble in absolute THF, acetonitrile, acetone, methanol, ethanol. Slightly soluble in absolute dioxane, benzene. Very insoluble in absolute petrolether, cyclohexane.

Upon standing in air or in contact with wet solvents, the N-tosyl imine hydrolyzes, giving triphenylstibine dihydroxide and p-toluenesulfonamide. By prolonged boiling in solvents containing water, the dihydroxide which initially forms is dehydrated to triphenylstibine oxide. If a long enough reaction time is allowed, only the oxide, and no dihydroxide, is found.

Reaction of Tris-(p-Tolyl)-Stibine Imine with p-Toluenesulfonyl Chloride

A solution of 2.63 gm tris-(p-tolyl)-stibine imine in 50 ml anhydrous, peroxide-free tetrahydrofuran was placed in a flask taking care to avoid contact with moisture. The imine had a nitrogen content of 3.20 percent, instead of the 3.41 percent in pure imine. Therefore, the actual weight of tris-(p-tolyl)-stibine imine used was 2.46 gm (6.0 mmole). A stoichiometric amount of anhydrous p-toluenesulfonyl chloride (0.78 gm = 4.5 mmole), dissolved in 10 ml anhydrous, peroxide-free THF, was added in a counter-current stream of nitrogen. A small amount of colorless precipitate separated. The mixture was stirred 30 minutes at room temperature, then 30 minutes at 55°C. The precipitate was filtered off under anhydrous conditions, purified by sublimation, and identified as ammonium chloride. Yield was 0.06 gm NH_4Cl (1.1 mmole); the maximum yield would be 1.5 mmole. Based on the reaction:

$$4(CH_3-C_6H_4)_3SbNH + 3\,ClSO_2C_6H_4-CH_3 \longrightarrow 3(CH_3-C_6H_4)_3SbN-SO_2C_6H_4CH_3 + (CH_3-C_6H_4)_3SbCl_2 + NH_4Cl$$

this represents a yield of 78 percent, calculated on the weight of pure imine used.

Upon evaporating the filtrate in vacuum under anhydrous conditions, a yellowish residue remained. This was extracted with four 15 ml portions of cold anhydrous, peroxide-free ether; a part of the residue dissolved. The residue obtained by evaporating the ether from the extracts and repeatedly recrystallizing from absolute alcohol/petrol ether had a melting point of 156°C and proved to be identical to tris-(p-tolyl)-stibine dichloride, as determined by mixed melting point, Debye X-ray, and Cl and Sb analyses. The yield was 0.51 gm (1.0 mmole), which represents 72 percent of the theoretical weight.

Analysis: Calculated for N, 2.48; S, 5.68; Cl, 15.21; Sb, 21.57. Found:N, 2.28; S, 5.52; Cl, 15.05; Sb, 21.4.

Reaction of Triphenylstibine Imine with Bromine

Fifty ml absolute, peroxide-free ether were added to 2.68 gm triphenylstibine imine dissolved in 10 ml absolute, peroxide-free tetrahydrofuran, taking care to avoid access of moisture. The imine had a nitrogen content of 3.55 percent (theory: 3.80%), so the actual weight of pure imine used was 2.49 gm (6.7 mmole). A stoichiometric amount of pure bromine (distilled over P_2O_5), 0.53 gm (3.35 mmole), was dissolved in 10 ml absolute, peroxide-free THF and added from a suction pipette to the imine solution at -70°C in a countercurrent stream of nitrogen. The bromine solution became decolored and a very insoluble colorless precipitate (A) formed.

After filtering off under anhydrous conditions and recrystallizing from absolute acetonitrile, 1.92 gm triphenylstibine-iminium bromide (4.2 mmole) were obtained. Melting point was 235° to 236°C (dec). The yield represents 28 percent more than would be expected from the amount of pure triphenylstibine imine used, based on the following reaction:

$$2\ Ph_3Sb{=}NH + X_2 \longrightarrow Ph_3SbNX + (Ph_3SbNH_2)X$$

The product was identified by mixed melting point and by Debye X-ray analysis. The yellow filtrate (B) obtained after removing the precipitate (A) was immediately evaporated at 5°C in vacuum under anhydrous conditions. The concentrated solution turned brown-red; upon cooling the solution to 0°C, yellowish needles precipitated. Several minutes after complete removal of solvent, the needles decomposed, turning first brown, then green. This residue showed no oxidizing power toward iodide in acid solution. Recrystallization from hot, absolute acetonitrile yielded 0.86 gm triphenylstibine-iminium bromide (1.9 mmole), melting at 235° to 236°C (dec). Addition of excess ether to the acetonitrile mother liquor at 0°C caused separation of about 150 mg triphenylstibine oxide, melting at 290° to 295°C.

Filtrate (B) initially contained an oxidizing agent, which could be shown by the action of the filtrate on a sulfuric acid solution of potassium iodide in aqueous acetonitrile. The iodine formed was titrated with sodium thiosulfate with starch indicator. The oxidizing value of 1 ml of filtrate (B), however, always lay under the theoretical value to be expected and sank rapidly to zero if the cold filtrate was allowed to stand, with simultaneous precipitation of more triphenylstibine-iminium bromide. The products of reaction with KI were triphenylstibine oxide, iodine, and ammonium bromide:

$$Ph_3SbNBr + 2\,HI + H_2O \longrightarrow Ph_3SbO + I_2 + NH_4Br$$

All these reaction products could be qualitatively detected by the following procedure: After removing the iodine with a few drops of 0.1 n sodium thiosulfate (starch indicator), the solution was evaporated to dryness. The triphenylstibine oxide contained in the dry residue was extracted with absolute THF. Ammonium bromide, remaining in the THF-insoluble residue, was separated by sublimation.

The continuing formation of triphenylstibine-iminium bromide in filtrate (B), as well as the fact that only the iminium bromide is recovered by rapid and careful evaporation of the filtrate to dryness can be explained by the reaction of solvent with the N-bromo-triphenylstibine imine initially formed. The solvent is dehydrogenated, forming unsatureated molecules; N-bromo-triphenylstibine imine takes up hydrogen, forming triphenylstibine-iminium bromide.

These conclusions are supported by the further observation that the filtrate (B), after standing a long time, can decolor additional quantities of bromine. Because of the reaction of N-bromo-triphenylstibine imine with the solvent, and because part of the iodine formed on addition of KI adds to the double bond in the dehydrogenated solvent, one finds too little iodine when titrating with sodium thiosulfate.

In the reaction of triphenylstibine imine with excess bromine and subsequent evaporation of filtrate (B), only an orange oil could be recovered, which could not be made to crystallize. Nor could N-bromo-triphenylstibine imine be isolated in solid form when absolute benzene or dioxane were used as solvent. Its transitory existence in solution, however, can be assumed highly probable.

Reaction of Triphenylstibine Imine with Iodine

Triphenylstibine imine (3.11 gm) was dissolved in 50 ml absolute, peroxide-free tetrahydrofuran. The imine had a nitrogen content of 3.54 percent (theory: 3.80%), therefore, the

actual amount of pure imine used was 2.88 gm (7.8 mmole). A stoichiometric amount of dry, sublimed iodine (0.98 gm = 3.9 mmole) was dissolved in 30 ml absolute, peroxide-free THF and added to the inine solution at -50°C in a countercurrent stream of nitrogen. The iodine was decolored and a very insoluble, light yellow precipitate (A) formed. This was removed by filtering under anhydrous conditions, and recrystallized several times from boiling, absolute acetonitrile, yielding 2.44 gm triphenylstibine-iminium iodide (4.9 mmole), melting point 217° to 218°C (dec). This quantity represents 26 percent more than would be expected from the amount of pure triphenylstibine imine used (100% yield = 3.9 mmole).

The yellow filtrate (B) obtained after removing the precipitate (A) was evaporated at 5°C in vacuum under anhydrous conditions, yielding an orange-red oil which could not be made to crystallize. Several days standing at -20°C merely caused separation of a very small amount of triphenylstibine-iminium iodide. The oily residue showed no oxidizing power with potassium iodide in acid solution (acetonitrile/water). It was not possible in this manner to isolate triphenylstibine-N-iodo-imine.

Reaction of Triphenylstibine Imine with Benzophenone

Apparatus: Schlenk Tube, oil-bath

Pure, dry benzophenone (2.0 gm) was melted under N_2 Schlenk tube, using an oil bath at 50°C. A small ampule of triphenylstibine imine was placed in the molten benzophenone and smashed. The weight of imine used was 1.2622 gm; its purity was 94 percent, therefore, the actual amount of pure inine was 1.186 gm (3.2 mmole). The impurity was triphenylstibine oxide. After breaking the ampule, the benzophenone melt turned brown, triphenylstibine imine dissolved, and a noticeable ammonia evolution was observed. The oil bath was removed after 4 to 5 minutes and the melt dissolved under anhydrous conditions in a solvent consisting of 20 ml absolute benzene and 10 ml absolute, peroxide-free tetrahydrofuran. By bubbling anhydrous hydrogen chloride through the solution, the diphenyl ketimine present precipitated as the colorless hydrochloride. This was filtered off under anhydrous conditions and sublimed under vacuum, using an oil bath temperature of 230° to 250°C. On the cold finger, 0.263 gm diphenyl ketiminium chloride, $\left[\phi_2C = NH_2\right]Cl$ (1.2 mmole), separated out. Based on the amount of pure imine used, this represents a yield of 38 percent of theory. The sublimate was identified by Cl and N analyses, and also by alkaline hydrolysis to ammonia and benzophenone:

$$\left[\phi_2C = NH_2\right]Cl + NaOH \longrightarrow \phi_2C = O + NaCl + NH_3$$

Repetition of the experiment with larger quantities gave diphenyl ketiminium chloride having, after sublimation, the following analyses.

Analysis: Calculated for: Cl, 16.28; N, 6.43. Found: Cl, 16.15; N, 6.34.

The residue obtained by evaporating the benzene filtrate to dryness in vacuum was recrystallized several times from a small amount of hot acetone by addition of water. Triphenylstibine oxide (1.107 gm = 3.0 mmole) was obtained, having a melting point of 290° to 295°C (dec). This was identified by converting to triphenylstibine diacetate with boiling glacial acetic acid; melting point 215° to 216°C; no mixed melting point depression.

Reaction of Triphenylstibine Imine with Phenylisocyanate

A total of 1.26 gm of 94 percent triphenylstibine imine (3.2 mmole actual imine) was dissolved in 30 ml absolute, peroxide-free THF. To this was added dropwise, in a countercurrent stream of nitrogen, 0.38 gm freshly distilled phenylisocyanate (3.2 mmole) in 10 ml absolute, peroxide-free THF. The solution turned yellow. After 10 minutes, the solvent was removed under anhydrous conditions and the residue subsequently dried two hours under high vacuum. There remained a yellow oil and a colorless solid. This was extracted with three, 30 ml portions of absolute, peroxide-free ether under anhydrous conditions. The oily substance was soluble, but the solid remained undissolved. The latter could be identified as triphenylstibine oxide, having a melting point of 290° to 295°C after recrystallizing from absolute benzene with absolute petrol ether. Identity was established by Debye X-ray and by conversion to triphenylstibine diacetate with boiling glacial acetic acid; melting point — 216°C. The raw yield was 1.22 gm.

The combined ether extracts were evaporated under anhydrous conditions, leaving behind a yellowish resin, which could not be made to crystallize and, therefore, was difficult to purify. The substance was quite soluble in alcohol, ether, benzene; it was insoluble in water.

It would be assumed that the resinous material was phenylcyanamide. Therefore, attempts were made to convert the material to identifiable, more easily recoverable derivatives. A small quantity of the oil was dissolved in a few drops of alcohol, several drops of water added and then, after 30 minutes, an excess of ether was added. A colorless precipitate formed, which was identified as phenylurea, ϕ-NH-CO-NH_2. It was soluble in alcohol; insoluble in ether and in water; melting point 146° to 147°C after recrystallization from a little water. An authentic sample of phenylurea was prepared from phenylisocyanate and ammonia:

$$\phi - N = C = O + NH_3 \longrightarrow \phi - NH - CO - NH_2 \qquad \text{(Reference 13)}$$

A mixed melting point with this sample showed no depression. The substance formed in the above hydrolysis:

$$\phi - NH - CN + HOH \longrightarrow \phi - NH - CO - NH_2 \qquad \text{(Reference 14)}$$

was heated to 160°C in a small sublimation apparatus. As is characteristic for monophenyl urea, the product decomposed to sym-diphenyl urea and urea:

$$2\,\phi - NH - CO - NH_2 \longrightarrow \phi NH\text{-}CO\text{-}NH\phi + H_2N - CO - NH_2 \qquad \text{(Reference 15)}$$

Sym-diphenyl urea sublimed above 170°C to form beautiful needles, melting at 238° to 239°C and showing no melting point depression when mixed with an authentic sample of sym-diphenyl urea. With hydrogen sulfide, the oily substance formed monophenyl thiourea:

$$\phi - NH - CN + H_2S \longrightarrow \phi - NH - CS - NH_2 \qquad \text{(Reference 16)}$$

For this reaction, a small quantity of the oily material was dissolved in a little warm benzene and H_2S passed through. There formed a precipitate very insoluble in water, ether, or benzene, but quite soluble in alcohol. Needles melting at 154°C were obtained after several recrystallizations from boiling water; they were identical to monophenyl thiourea (prepared from phenyl isothiocyanate and ammonia):

$$\phi - N = C = S + NH_3 \longrightarrow \phi - NH - CS - NH_2 \quad \text{(Reference 17)}$$

Melting point of the mixture showed no depression. These results show that the oily product was phenylcyanamide.

Reaction of Triphenylstibine Imine with Phenyl Isothiocyanate

A total of 1.40 gm of 95 percent triphenylstibine imine was dissolved in 20 ml absolute, peroxide-free THF (3.6 mmole actual imine). The impurity was triphenylstibine oxide. To this was added dropwise, in a countercurrent stream of nitrogen, 0.48 gm pure, freshly distilled phenyl isothiocyanate (3.6 mmole) in 2 to 4 ml absolute, peroxide-free THF. The mixture turned yellow and then gradually dark brown. After standing two hours at room temperature, the solution was evaporated in vacuum, then completely dried for one hour in high vacuum, leaving as residue a brown, viscous mass. This was extracted with two 20 ml portions of ice cold absolute, peroxide-free ether. A yellowish, ether-insoluble solid remained; the viscous, greasy material dissolved in the ether, giving a brown solution. The solid was recrystallized several times from a small amount of absolute benzene by adding absolute petrol ether; after a subsequent recrystallization from alcohol, the melting point was 120°C. The product was identical to triphenylstibine sulfide; a mixed melting point with authentic material showed no depression.

The combined ether extracts were evaporated to dryness in vacuum under anhydrous conditions, leaving a brown mass which was insoluble in water, but quite soluble in alcohol and benzene. Since it could be assumed that this residue contained phenylcyanamide, attempts were made to convert it to more easily identifiable derivatives.

Hydrolysis yielded monophenyl urea: a few drops of water were added to a concentrated solution of the substance in a small amount of alcohol. After standing 20 minutes, an excess of cold ether was added, causing separation of a precipitate which was very insoluble in water and ether, but quite soluble in alcohol. After recrystallization from a small amount of water, the melting point was 147°C. The compound was identical to monophenyl urea. An authentic sample was prepared from phenylisocyanate and ammonia. The mixed melting point showed no depression.

The substance reacted with hydrogen sulfide to give monophenyl thiourea: H_2S was passed through a concentrated solution of the material in benzene. A precipitate formed which was only very slightly soluble in water, ether, and benzene, but quite soluble in alcohol. After repeated recrystallization from boiling water, the melting point was 154°C. The product was identical to monophenyl thiourea. In mixture with an authentic sample made from phenyl isothiocyanate and ammonia, the melting point showed no depression. These reactions may be taken as proof that phenylcyanamide was present.

Reaction of Triphenylstibine Imine with Acetyl Chloride

A total of 2.28 gm of 95 percent triphenylstibine imine was dissolved in 30 ml absolute, peroxide-free THF (5.8 mmole actual imine). The impurity was triphenylstibine oxide. To

this was added, in a countercurrent stream of nitrogen, a solution of 0.45 gm pure, freshly distilled acetyl chloride (5.8 mmole) in 5 ml absolute, peroxide-free THF at -20°C. A very insoluble, colorless precipitate immediately separated. This was filtered off under anhydrous conditions and recrystallized from hot, absolute acetonitrile, yielding 1.05 gm triphenylstibine-iminium chloride (2.6 mmole), melting at 232°C (dec); maximum yield = 2.9 mmole. The iminium chloride was identified by Debye X-ray analysis and by mixed melting point.

The reaction filtrate, after removing the precipitate, was evaporated to dryness in vacuum under anhydrous conditions. A yellowish, semisolid residue remained. After repeated extraction with absolute ether and absolute cyclohexane there remained a colorless, very insoluble powder, which proved identical to triphenylstibine oxide. Melting point was 290° to 295°C after recrystallization from acetone with water. Identification was made by converting to triphenylstibine diacetate with boiling glacial acetic acid. The yield of triphenylstibine oxide was 1.12 gm (3.0 mmole). The maximum yield, based on the amount of pure imine used, would have been 2.9 mmole, but the isolated oxide included the amount brought in with the starting material. Small amounts of ammonium chloride and acetamide formed as by-products in the reaction. Amonium chloride precipitated with the triphenylstibine-iminium chloride and could be separated from the latter by recrystallization from absolute acetonitrile. Acetamide was recovered from the ether and cyclohexane extracts through evaporation of the solvents.

In order to check for the formation of acetonitrile in the reaction of triphenylstibine imine with acetyl chloride, the experiment was repeated as already described. After reaction, the liquid phase (tetrahydrofuran + acetonitrile + acetyl chloride) was distilled under vacuum. The distillate was examined gas-chromatographically. Acetonitrile was clearly present, along with tetrahydrofuran. The acetyl chloride also present caused no interference in the separation.

Reaction of Triphenylstibine Imine with Elemental Sulfur

To a solution of 1.21 gm triphenylstibine imine (3.2 mole) in 25 ml absolute, peroxide-free tetrahydrofuran was added, in a countercurrent stream of nitrogen, 0.82 gm dry, pure sulfur (3.2 mmole). After discharge of the initial blue coloration, the mixture was allowed to stand two hours more at room temperature. The clear, amber supernatant liquid was then analyzed by means of vertical paper chromatography (Reference 17).

Paper	2040 a Schleicher and Schüll
Paper treatment	impregnation with dimethylformamide, drying
Carrier	methanol
Time	6 to 8 hours
Development	the dry chromatogram was drawn through 0.1 n $AgNO_3$ and then dried.

With silver nitrate, S_7NH gives a sharp brown-black spot. All other sulfur-nitrogen compounds migrate appreciably slower, so S_7NH is not obscured. Only sulfur tenaciously moves along with S_7NH, but it produces no coloration in the development with silver nitrate. Pretreatment of the paper with dimethylformamide is not absolutely necessary; the S_7NH then migrates together with the sulfur on the solvent front, whereas the other sulfur-nitrogen compounds remain behind. Comparison substances used were S_7NH, S_4N_4, and $S_4N_4H_4$. The chromatogram showed conclusively the presence of S_7NH and absence of all other sulfur-nitrogen compounds.

The remaining reaction solution was separated from excess sulfur and evaporated in vacuum to dryness under anhydrous conditions. The residue was extracted several times with warm, absolute benzene. After filtration and concentration of the extract at -20°C, an excess of petrol ether was added, causing a precipitate to form. The latter was then reprecipitated from a small amount of carbon disulfide by addition of petrol ether, and finally recrystallized from alcohol/petrol ether. Needles formed, melting at 120°C. The product proved to be identical to triphenylstibine sulfide. Yield was 0.69 gm (1.7 mmole), 56 percent of theory. Identification was by means of Debye X-ray analysis and by mixed melting point.

During the entire reaction there was no gas evolution whatsoever. Neither nitrogen nor ammonia formed. Tests for hydrazine and hydroxylamine were also negative.

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13. ABSTRACT

The following bi-functional compounds were synthesized as starting materials for the synthesis of inorganic polymers with sulphur-nitrogen-carbon bonds: Sulfuryl-diisocyanate, $O_2S(NCO)_2$; amidosulfuric acid isocyanate, H_2NSO_2NCO; chlorosulfuryl-isocyanate, $ClSO_2NCO$; fluorosulfuryl-isocyanate, FSO_2NCO; imido-bis-sulfuric acid chloride, $HN(SO_2Cl)_2$, and imido-bis-sulfuric acid fluoride, $HN(SO_2F)_2$. The polyaddition of diamines and diols with $O_2S(NCO)_2$ results in polymers which are not very stable to temperature and hydrolysis. The polymers found by reaction of H_2NSO_2NCO with urea and sulfamide, $O_2S(NH_2)_2$, likewise, are not very stable.

In the field of the phosphorus-nitrogen-compounds the synthesis of triphenyl-phosphine imines and of N-halogen-phosphine imines is described. The reaction of halogen-imines with triply-bounded phosphorus derivatives is leading to compounds with the system of $\geq P-\underline{N}-P\leq$. Further experiments deal with antimony-nitrogen compounds and their reactions.

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